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GENERAL INTRODUCTION

American Chemical Society's Series of Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on Chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical progress. The American Chemical Society named as Trustees, to make the necessary arrangements of the publication of the Monographs, Charles L. Parsons, secretary of the Society, Washington, D. C.; the late John E. Teeple, then treasurer of the Society, New York; and the late Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the ACS Series of (a) Scientific and (b) Technological Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successor) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this sketch) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first Monograph of the Series appeared in 1921. After twenty-three years of experience certain modifications of general policy were indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. By 1944 this differentiation was fast becoming nebulous. Research in private enterprise had grown apace and not a little of it was pursued on the frontiers of knowledge. Furthermore, most workers in the sciences were coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and frankly recognize that their objectives are common, namely, the search for new knowledge for the service of man. The officers of the Society therefore combined the two editorial Boards in a single Board of twelve representative members.

Also in the beginning of the Series, it seemed expedient to construe rather broadly the definition of a Monograph. Needs of workers had to be recog-

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nized. Consequently among the first hundred Monographs appeared works in the form of treatises covering in some instances rather broad areas. Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the Monograph character, which means more complete and critical treatment of relatively restricted areas, and, where a broader field needs coverage, to subdivide it into logical subareas. The prodigious expansion of new knowledge makes such a change desirable.

These Monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline; second, to stimulate further research in the specific field treated. To implement this purpose the authors of Monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.

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FOREWORD

In this age of modern living, specialization is the order of the day. This is true in all fields of human endeavor, particularly in chemistry with its vast and ever mounting array of knowledge being gained through research. Textbooks of a general nature have become quite elementary by comparison with the extent of the available knowledge on the subject. As a result, these general texts are rapidly giving way to individual volumes or sets of volumes devoted exclusively to much smaller segments of chemistry or of chemical industry. Many of the individual elements have been covered by separate monographs, while a large number of specific reactions and special classes of chemical compounds have likewise received individual attention by authors in recent years. And so, it is timely for the field of perchloric acid and the perchlorates to be made the exclusive subject of a detailed and comprehensive review. This book, therefore, is intended to provide such coverage, and should prove useful in both academic and industrial spheres of activity.

Uses for perchlorates and perchloric acid have been developed only in rather recent years. From their discovery early in the nineteenth century until about fifty years ago, these compounds were merely names in comprehensive inorganic texts, and even professors of inorganic chemistry seemed to be unfamiliar with their properties or possible uses. For a number of years, only potassium perchlorate was obtainable in this country, but this salt is unsuited for making perchloric acid or other perchlorates, due mainly to its very limited solubility, and this helped to retard the study of these other compounds.

Also, it had apparently been the general belief among chemists of the day that the addition of another oxygen atom to the chlorate radical should make perchlorates and perchloric acid more unstable than chlorates and chloric acid. Thus, it was not until after the remarkable stability of perchlorates had become more widely known that various possible uses for these compounds began to be explored.

Research gradually developed satisfactory methods for the preparation of perchloric acid and the various perchlorates. These methods in turn helped to illustrate the unusual stability of the ClO_4^- ion; the acid resists aqua regia and it can be distilled (under reduced pressure) without decomposition. Also, it is not reduced by nascent hydrogen or, at the cathode, by electrolysis. This stability is something that was entirely unexpected of any combination of chlorine and oxygen. Of course, it must not be forgotten, however, that perchlorates are powerful oxidants and must be handled with due caution. As suppliers of oxygen, they are used

in contact with organic materials as explosives, and as a source of oxygen for missile propellants.

Perchlorates reverse the general rule of solubility since almost all perchlorates are very soluble except those of potassium, rubidium and cesium which are insoluble, or only slightly soluble. Furthermore, the heavy metal perchlorates are much less subject to hydrolysis than other salts of the same metals, and their high solubilities have been utilized in a number of applications, as in electroplating. Perchloric acid has found extensive use in analytical work in place of sulfuric acid, while the alkaline earth perchlorates are becoming widely used as drying agents.

It seems logical to assume, therefore, that still other important developments in the manufacture and use of perchlorates and perchloric acid can be expected in the years to come. Past experience has shown that the last word has never been spoken regarding developments in any field. Might not someone find THE catalyst that would speed up the miserably slow change of chlorine and oxygen over water into perchloric acid?

Such a discovery would constitute a major "breakthrough" in perchlorate chemistry, and it is believed that this book should be a good "thought-producing" source of ideas for research in both this and other directions.

F. C. MATHERS

*Indiana University
Bloomington, Indiana
July, 1960*

PREFACE

The purpose of this monograph is to provide a comprehensive survey and review of the vast accumulation of knowledge on the subject of perchlorates, including perchloric acid. This work, which has continued in progress up to the present time, was first started in 1942 in an effort to assemble a complete reference file to be used in a research and development program at Western Electrochemical Company (now American Potash & Chemical Corporation). It is presented from the point of view of the manufacturer interested primarily in finding and developing novel, economical and safe methods of manufacture, handling and use of these interesting, important and useful compounds.

It is hoped that this presentation will serve to stimulate more interest and hasten progress in research on the preparation and use of perchlorates.

I wish to acknowledge the important contributions made by the following members of the Research Staff of American Potash & Chemical Corporation.

EDYTHE MOORE, Head of Technical Information Center at the Whittier Research Laboratory, and her assistants, for providing the literature survey, obtaining articles and translations, and for the task of indexing.

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WILLIAM H. HILL, Assistant Research Professor, Department of Occupational Health, University of Pittsburgh, for their critical review of Chapter 10.

JOSEPH C. SCHUMACHER

Los Angeles, California
July, 1960

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1. HISTORY

The discovery of potassium perchlorate was reported in Germany in 1816 by Count Friederich von Stadion⁶¹ of Vienna. He fused a small quantity of potassium chlorate in a retort and then carefully added a small amount of sulfuric acid. Chlorine dioxide was given off and the residue was identified as a mixture of potassium sulfate and a difficultly soluble salt which he identified as potassium perchlorate.

In the course of identifying the composition and structure of this new salt, von Stadion⁶⁰ prepared perchloric acid by electrolyzing a saturated aqueous solution of chlorine dioxide and also by distilling the new acid from a heated mixture of sulfuric acid and potassium chlorate. He also prepared potassium perchlorate by (1) neutralizing perchloric acid with potassium hydroxide and (2) electrolyzing a saturated solution of potassium chlorate between platinum electrodes.

In addition to his important discoveries relating to the preparation and identification of perchloric acid and potassium perchlorate, von Stadion recognized the importance of electrochemistry as an effective means of synthesis.

In 1830, Serullas⁵¹ reported his discovery of a new method of preparing perchloric acid. He observed that during the distillation of chloric acid, one part splits into chlorine and oxygen and that another part, almost one-third of the chloric acid employed, is converted to perchloric acid. He also observed that perchloric acid is very stable and may be distilled at an elevated temperature without decomposition.

In 1831, Serullas⁵⁴ reported his discovery of a new method of transforming potassium chlorate into potassium perchlorate. When he had first noted an almost insoluble salt-like residue remaining upon the incomplete decomposition of potassium chlorate by heat, he attributed it to cohesion. It seemed improbable to him that earlier investigators had neglected to ascertain what actually took place. Later he identified the residue as potassium perchlorate.

Serullas observed that the formation of potassium perchlorate by the action of sulfuric acid on the chlorate, and the formation of perchloric acid by the simple boiling of concentrated chloric acid are comparable reactions. This observation led him to believe that the simple action of elevated temperature, maintained between certain limits, causes potassium chlorate to pass to the state of perchlorate when part of the oxygen is transferred to the undecomposed chlorate.

Having thus found a simple method of preparing potassium perchlorate,

he proceeded to develop a new method of preparing perchloric acid, from potassium perchlorate and fluosilicic acid. He mixed potassium perchlorate and hydrofluosilicic acid and then evaporated the resulting solution; this was followed by cooling to precipitate potassium fluosilicate.

Continuing his research with perchloric acid, Serullas⁵³ prepared ammonium perchlorate and a number of metal perchlorates. During the course of this work his attention was attracted toward the remarkable difference that exists between the solubility of potassium perchlorate and that of sodium perchlorate. This difference suggested to him a valuable method of distinguishing between these two alkali metal ions and a means of separating them.

Serullas⁵¹ can also be credited with popularizing the use of the term "perchlorate" as distinguished from the term "oxychlorate" used by von Stadion and others during the period between 1816 and 1831. Serullas used the terms interchangeably in his papers, and thereafter the word "perchlorate" was used almost exclusively, if not entirely.

Following the important discoveries of von Stadion, and later those of Serullas, a continuing and almost constant effort was made by a large number of investigators to characterize and find new methods of preparing and using perchloric acid and its salts. This effort was motivated to a large extent by scientific curiosity, but also by a desire to utilize these substances in a variety of ways in analytical chemistry, and as an ingredient in explosives, pyrotechnics and rocket propellants.

With regard to the characterization of perchlorates, von Stadion's determination of the composition of potassium perchlorate was confirmed by Mitscherlich,³⁷ Serullas,⁵³ and Marignac.³⁴ Roscoe⁴⁵ later prepared and identified perchloric acid in three forms: namely, the anhydride, the monohydrate—a solid crystalline substance which had been discovered by Serullas but not identified by him—and the dihydrate, a constant boiling liquid. Roscoe also pointed out that the anhydride, Cl_2O_7 , had not been isolated, and almost 40 years elapsed before Michael and Conn³⁵ succeeded in preparing and isolating it. In 1902, van Wyk⁷⁰ studied the relationship of freezing point versus composition and was thus able to identify five hydrates of perchloric acid.

Studies on the structure of perchloric acid were carried out by Volmer,⁶⁷ Smith and Goehler⁵⁹ and later, by Fonteyne.¹⁹ Volmer used x-ray techniques. Smith and Goehler used a melting point-density relationship technique. Fonteyne employed Raman spectra.

Earlier in 1881, Berthelot⁶ had studied the thermochemistry of chlorates and perchlorates and showed that the transformation of potassium chlorate to potassium perchlorate is exothermic. This led him to observe that the perchlorates are considerably more stable chemical compounds than the corresponding chlorates.

The curious fact of the occurrence of perchlorate in the natural deposits of nitrates in Chile was first reported by Beckurts⁴ in 1886. Following this discovery, damage to grain crops in Belgium was laid to the perchlorate present in the Chilean nitrate used as plant food.^{33, 56-58, 66} To this day the question as to the origin of this naturally occurring perchlorate remains unanswered. However, in this connection, small amounts of perchlorate have been reported quite recently³ in sea water, as well as in a number of natural brines and saline deposits in Australia and elsewhere. It has been suggested that such natural occurrences may be caused by the action of microorganisms, but one can also speculate on a purely chemical mechanism. In either case a possible new method of producing perchlorates is suggested.

A series of compounds in which nitrogen oxides and perchlorate are combined have been prepared, beginning with the discovery of nitrosyl perchlorate, $(\text{NO})^+(\text{ClO}_4)^-$, by Hofmann and Zedtwitz²⁵ in 1909. Hantzsch and his co-workers,²¹ in 1928, found that when dry nitric and perchloric acids were mixed in various proportions, two different compounds were formed. They were named nitracidium perchlorate, $[\text{O}:\text{N}(\text{OH})_2]^+\text{ClO}_4^-$, and hydronitracidium perchlorate, $[\text{N}(\text{OH})_3]^{++}(\text{ClO}_4)_2^-$. In 1940 Gordon and Spinks²⁰ discovered nitroxyl perchlorate, NClO_6 , or $(\text{NO}_2)^+\text{ClO}_4^-$.

In 1947, Rohrback and Cady⁴⁴ identified fluorine perchlorate, FClO_4 , which they prepared from fluorine and perchloric acid. Another compound, perchloryl fluoride, FClO_3 , was prepared by Bode and Klesper⁸ in 1951, by fluorinating potassium chlorate.

Hofmann and his co-workers²³ in 1906 began studies of compounds formed when aqueous perchloric acid (72 per cent) is added to various organic compounds including alcohols, amines, ketones. Most or all of these compounds were thermally unstable and would detonate on heating. Hofmann²⁴ found that perchloric acid offers advantages over picric acid for separation of carbinols, ketones and amines from the resinous materials formed during their preparation. He concluded that perchloric acid apparently does not add to double bonds. He also found that perchloric acid has very slight oxidizing power under the conditions employed because pyrogallol or hydroquinone may be recrystallized from a mixture of perchloric and acetic acids. He prepared esters of epichlorhydrin and perchloric acid, compounds he found to be more explosive than nitroglycerine.²⁶

Other than Kolbe's verification³² of von Stadion's early work on electrolysis of chlorate to perchlorate, at which time he also confirmed Berzelius²⁷ preparation of aqueous acid by the electrolysis of chloric acid solution, little work was done on the electrolytic methods of production and use until about 1890. In that year, Oscar Carlson, founder and president of Stockholms Superfosfat Fabriks AB (Fosfatbolaget), applied for a

patent for diaphragmless electrolytic cells for the production of sodium chlorate.¹³ The formation of perchlorate was observed. Research to find conditions favorable to perchlorate formation was intensified in the laboratory and in the pilot plant which Fosfatbolaget built in 1892. A commercial plant was constructed in 1893 at Mansbo, Sweden, and in 1898, small quantities of ammonium perchlorate were produced, but with variable results. Sometimes a bath of sodium chlorate solution could be oxidized to perchlorate in 5 or 6 days; other times the process lasted many weeks. By 1904, production was running smoothly; potassium perchlorate was first manufactured at Mansbo in 1905.⁶²

Meanwhile, Carlson had been experimenting on the production of explosives containing ammonium perchlorate; in 1897 he received a patent in this field¹²; the well-known explosive "Carlsonsit" was later developed and covered by many patents.

Following Sweden's pioneering work, France, Germany, Switzerland and the United States also began to produce perchlorates. In 1901, potassium, sodium and ammonium perchlorates were produced electrolytically at Chedde, France. Gesellschaft für elektrochemische Industrie Turgi (now Elektrochemie Turgi) began manufacturing potassium perchlorate in Switzerland, in 1907.¹⁵ Oldbury Electro-Chemical Company (now Hooker Electrochemical Company) began experimental work on the electrolysis of sodium chlorate using platinum anodes, producing sodium perchlorate in 1908; by 1910 potassium perchlorate was produced at the rate of 150 tons per year at their plant at Niagara Falls, New York.²⁷

Until the first World War broke out, however, the total volume of perchlorate production in the world was not more than 2,000 to 3,000 tons per year. The lack of nitric acid during the war forced Germany to promote the development of perchlorates, and the factory of Chemical Works Griesheim Elektron at Bitterfeld produced about 20,000 tons during the war years.¹⁴ Elektrochemie Turgi also manufactured ammonium perchlorate, in addition to sodium and potassium perchlorates, at their Spreitenbach factory.¹⁵ Fosfatbolaget, in 1915, erected a second plant with a capacity of 750 tons of ammonium perchlorate and 475 tons of potassium perchlorate a year. This plant, in Trollhatten, is today the main producer of sodium chlorates and perchlorates in Sweden.⁶²

After the first World War, commercial production decreased to a minimum. There was no very significant new demand for the perchlorates, other than for use in fireworks, railway signals, etc., until the late 1930's and during World War II, when the present major interest began.

Canada produced perchlorates during the years 1942 to 1946. At that time Electric Reduction Company of Canada built facilities at Buckingham, Quebec, to produce ammonium, barium and potassium perchlorate for military use.¹⁰

Potassium perchlorate was placed on the list of strategic chemicals in the United States in 1940 and production was stepped up, increasing 20-fold, reaching about 20,000 tons per year during the years 1941-1945. The number of domestic manufacturers increased from one to four; the three new producers built four new plants.

Beginning in 1941, the Cardox Corporation, to take care of its own needs for potassium perchlorate in the mining field, produced potassium perchlorate at its Claremore, Oklahoma plant. In 1943, they constructed and operated for the Government another potassium perchlorate plant at the same location.¹¹ Vick Chemical Company built a plant in 1943 for the production of ammonium perchlorate in Greensboro, North Carolina.

In 1942, Western Electrochemical Company, now American Potash & Chemical Corporation, built the first West Coast electrolytic potassium perchlorate plant at Los Angeles, California. Support was received for this program from the Guggenheim Aeronautics Laboratory at the California Institute of Technology. Various perchlorates were prepared for experimental production of rocket propellants. Soon thereafter Aerojet Engineering Corporation, now Aerojet General Corporation, started commercial production of rocket motors. Thus a new and increasing demand for perchlorates was established.

In 1945, Western Electrochemical Company took over some of the installations of Basic Magnesium Inc., Henderson, Nevada, and converted them into a perchlorate manufacturing plant to satisfy the needs of the military rocket program. Immediately following World War II the demand for perchlorates began to shift from potassium to the ammonium salt. Also at this time Thiokol Chemical Company, and others, started to manufacture solid rocket propellants.

In 1948, Western Electrochemical Company built an ammonium perchlorate pilot plant at Henderson, Nevada. In 1951, acting as prime contractor for the Navy and Army, Western Electrochemical Company initiated a program leading to the design and construction of an ammonium perchlorate plant with a capacity many times greater than any other plant. The plant started production in 1953 and has been in operation, although at less than full capacity, since start-up. In 1958, increased interest in solid propellants created new demands for perchlorates and a new round of expansion was started. H.E.F. Inc., (owned by Hooker Electrochemical and Foote Mineral), and also Pennsalt Chemicals Corporation, have announced plans for construction of new perchlorate facilities. American Potash & Chemical Corporation, the largest producer of perchlorates, has also announced plans for increasing production.

Many improvements and modifications in the electrolysis of chlorates to perchlorates, in efforts to increase yields, have been demonstrated. When the electrolytic process was adapted for use in the commercial production

of perchlorates, speculation arose as to what reactions actually took place at the anode in chlorate electrolysis. Foerster,¹⁸ in 1897, and Winteler,⁶⁹ in 1898, reported their investigations to determine conditions under which perchlorate is obtained with maximum current yield. Winteler stated that either platinum or superoxide electrodes could be used, although he did not specify the nature of the superoxide. Both Foerster and Winteler observed the evolution of ozone during the electrolytic formation of perchlorate, especially from concentrated solutions.

In 1903, Oechsli³⁹ proposed that the reaction is not a direct addition of oxygen to ClO_3 , with the formation of ClO_4 . It is rather a secondary reaction involving the discharge of the chlorate ion followed by reaction of the free radical with water in the vicinity of the anode, forming chlorous and perchloric acids and liberating oxygen; the unstable chlorous acid then spontaneously oxidizes to chloric acid.

Bennett and Mack⁵ took exception to Oechsli's theory in 1916, when they attempted to show that chlorates may be oxidized to perchlorates by persulfuric acid, ozone or hydrogen peroxide. They cited Schoch's experiments to show that perchlorates are formed at the anode at a potential far below that necessary for the continuous discharge of any ions present in the solution.

Later, in 1920, Knibbs and Palfreeman,³¹ considering that neither of these theories were adequate, presented their own theory, a modification of Oechsli's, maintaining that perchlorate formation is due to chlorate ion discharge, but that the reactions taking place subsequently are analogous to those in the formation of persulfate.

In 1953, Sugino and Aoyagi⁶⁴ actually measured polarographically the current-potential curves for the electrolytic oxidation of chlorate. This mechanism assumed the discharge of the chlorate ion and subsequent hydrolysis.

At the University of Texas, in 1955, Philipp and Morgan⁴³ observed the similarities between conditions favorable to the electrolytic and to the chemical oxidation of aqueous chlorates, the same factors in each process favoring high yields. They postulated that the mechanism for the electrolytic formation of perchlorates involves an unusually high valence oxide which forms on the anode surface. In the highly acidic conditions existing there, the oxide is unstable and reacts similarly to higher oxides in chemical oxidation experiments.

There has been no general agreement on the mechanism of the electrolytic formation of perchlorate. This suggests additional studies of the mechanism, using lead dioxide anodes and also the chemical oxidation in aqueous acid and neutral solutions, using oxidizing agents such as the platinum superoxide of Philipp and Morgan, or lead dioxide of the type suitable for electrolytic work.

Until recently, platinum has been the most favored anode material, in spite of its high initial cost and losses during operation. However, the search for a substitute for platinum has been under way almost from the time that electrolytic production of perchlorates was begun commercially.

Ferchland¹⁷ patented a process for preparing a lead dioxide anode in 1905. Schoch and Randolph⁴⁹ made a study of the behavior of iron and nickel cathodes in 1910. Huth²⁹ patented a process for producing an anode of crystalline manganese dioxide embedded with pieces of lead dioxide; in 1919, Sato⁴⁷ produced an anode of iron oxide, clay and sodium nitrate.

Howard²⁸ was unsuccessful in his attempts to oxidize sodium chlorate to perchlorate using a magnetite anode. In 1934, Angel¹ investigated the use of tungsten and molybdenum anodes, but later that same year, Angel and Mellquist² deposited lead dioxide on iron-, steel-, copper- and silver-plated sheets. It was Kato and Koizumi³⁰ who applied their lead dioxide anode, made more compactly by the addition of a colloidal matter, to the successful production of perchlorates. In 1939, Sugino, Koizumi and Kitahara⁶⁵ patented a process for preparing perchlorates using a lead dioxide anode and a cathode of gold, silver, platinum or rhodium. Shibasaki in 1948 pressed and molded an anode of powdered lead dioxide and vinyl chloride.⁵⁵

Mizuguchi³⁸ studied the surface processes which take place on lead dioxide anodes during electrolytic oxidation and suggested the addition of hydrofluoric acid to decrease this activity.

In 1950 Sugino⁶³ outlined new methods for the production of lead dioxide anodes by the electrolytic deposition of lead dioxide from a neutral lead nitrate solution upon (1) the inner surface of an iron or nickel cylinder, or (2) the outer surface of a soft and nonmetallic conductor, such as a rod with a surface of a paraffin-graphite mixture.

In 1951, Pennsalt received a research contract from the Office of Naval Research to explore alternate anodes to replace platinum; they evolved a lead dioxide anode made by the electrodeposition of lead dioxide from a lead nitrate bath onto tantalum, which was demonstrated to the Office of Naval Research in January, 1954.⁴⁰

American Potash & Chemical Corporation, also under contract to the Navy, designed, constructed and operated successfully a pilot plant cell in which lead dioxide anodes were used.

Although all the present commercial producers of perchlorates now employ the electrolytic process, it is conceivable that a commercial non-electrolytic process may be developed in the future to meet the growing demands for perchlorates.

CHRONOLOGY

- 1816** von Stadion reported his discovery of potassium "oxychlorate" (perchlorate) and "oxygenated chloric acid" (perchloric acid).⁶⁰
- 1830** Serullas prepared perchloric acid by thermal decomposition of chloric acid.⁵¹
- 1831** Serullas prepared:
1. Aqueous perchloric acid by chemical reaction of potassium perchlorate and fluosilicic acid.⁵⁴
 2. A solid form of perchloric acid, later identified as the monohydrate.⁵²
 3. Potassium perchlorate by thermal decomposition of potassium chlorate.⁵⁴
- Serullas devised the perchlorate method for the separation of potassium and sodium.⁵³
- 1835** Berzelius prepared aqueous perchloric acid by electrolysis of chloric acid solution.⁷
- 1840** Penny prepared aqueous perchloric acid by chemical reaction of chlorate with nitric acid.⁴¹
- 1841** Hare and Boye prepared the ethyl ester of perchloric acid.²²
- 1843** Millon observed that aqueous solutions of chlorine dioxide, ClO_2 , in light, decomposed into chlorine and perchloric acid.³⁶
- 1847** Kolbe prepared perchloric acid by electrolysis of hydrochloric acid solution.³²
- 1862** Roscoe prepared anhydrous perchloric acid and identified the solid acid obtained by Serullas as the monohydrate.⁴⁵
- 1871** Schloesing prepared sodium perchlorate by thermal decomposition of sodium chlorate and transformed sodium perchlorate to ammonium perchlorate by the addition of ammonium chloride.⁴⁸
- 1874** Fairley prepared perchloric acid or a perchlorate by passing ozonized air through a solution of hypochlorous acid or sodium hypochlorite.¹⁶
- 1881** Berthelot showed how thermochemistry accounts for the characteristic properties of the perchlorates, pointing out that the change of potassium chlorate to perchlorate by heat is exothermic.⁸
- 1886** Beckurts discovered perchlorate in nature in Chilean saltpeter.⁴
- 1890** Carlson patented an electrolytic process using cells without diaphragms for the manufacture of chlorate and perchlorate.¹³
- 1893** First commercial perchlorate plant constructed at Mansbo, Sweden.⁶¹
- 1895** Carlson started experiments on the production of explosives containing ammonium perchlorate.¹²
- 1897** Foerster studied the electrolytic formation of perchlorate to determine most favorable conditions.¹⁸
- 1898** Winteler observed the formation of ozone during electrolysis of concentrated aqueous perchlorate solutions.⁶⁹
- 1900** Michael and Conn isolated the anhydride of perchloric acid, Cl_2O_7 .³⁵
- 1902** Van Wyk identified five hydrates of perchloric acid.⁷⁰
- 1903** Oechsli presented a theory for the mechanism for electrolytic formation of perchlorate postulating discharge of the chlorate ion.³⁹
- 1905** Ferchland patented a process for preparing lead dioxide anodes.¹⁷
- 1906** Hofmann and his co-workers prepared perchlorates of many organic compounds.²³
- 1908** Borelli prepared the complex mercury cyanide perchlorate, $(\text{HgCN})\text{ClO}_4$.⁹
- 1909** Hofmann and Zedtwitz prepared nitrosyl perchlorate.²⁵
- 1911** Salvadori prepared various complexes of cobalt and perchloric acid.⁴⁶
- 1916** Bennett and Mack presented a theory of the electrolytic formation of perchlorate postulating the direct addition of oxygen to the chlorate.⁵

- 1920 Knibbs presented his theory of electrolytic formation of perchlorate postulating chlorate ion discharge followed by chemical reactions in a mechanism similar to that of persulfate formation.³¹
- 1921 Weinland isolated anion complex perchlorate salts.⁶⁸
- 1928 Hantzsch and Berger prepared nitronium perchlorate, $(\text{H}_2\text{O}_2\text{N})\text{ClO}_4$, from absolute perchloric acid and absolute nitric acid.²¹
- 1934 Angel and Mellquist substituted lead dioxide anodes for platinum in electrolysis of chlorates.²
- 1936 Fonteyne began studies of the structure of perchloric acid employing Raman spectra.¹⁹
- 1939 Sugino, Koizumi, and Kitahara patented process for preparing perchlorates by electrolysis using a lead dioxide anode.⁶⁵
- 1940 Gordon and Spinks reported the discovery of nitroxyl perchlorate, NClO_4 .²⁰
- 1942– New military uses for perchlorates caused manifold expansion of the industry
- 1945 in the United States and Canada.
- 1946 Pernert patented a perchloric acid process based on the chemical reaction of sodium perchlorate and hydrochloric acid.⁴²
- 1947 Rohrback and Cady reported discovery of fluorine perchlorate, FClO_4 .⁴⁴
- 1951 Bode and Klesper reported the discovery of perchloryl fluoride, FClO_3 .⁸
- 1953 Sugino and Aoyagi measured the anodic potential of perchlorate formation and presented a theory of the mechanism of reaction.⁶⁴
- 1955 Philipp and Morgan proposed a theory of the mechanism of electrolytic formation of perchlorate postulating a high valency platinum oxide intermediate.⁴³
- 1956 Schumacher patented ammonium perchlorate process based on continuous reaction of liquid anhydrous ammonia, a mineral acid and sodium perchlorate.⁶⁰
- 1958 New expansion of perchlorate industry began.

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2. PERCHLORIC ACID

ANHYDROUS PERCHLORIC ACID

Preparation

Anhydrous perchloric acid can best be prepared by vacuum distillation from a mixture of fuming sulfuric acid and commercially available 72 per cent perchloric acid. Smith⁴⁸ reports that 75 per cent yields of anhydrous perchloric acid may be obtained in this way by distillation at pressures of 1 mm or less from a mixture of four volumes of oleum to one of 72 per cent perchloric acid.

The anhydrous acid is a clear, colorless, mobile liquid with a viscosity of 0.76 centipoises at 20°C and 0.563 centipoises at 50° as determined by Van Wyk.⁷⁰ The liquid is unstable at ordinary temperatures, slowly developing a yellowish to brown color and becoming explosive. The electrical conductivity of aqueous solutions has been studied by Usanovich and Sumarokova⁶² and found to decrease rapidly from 0.7828 at 10 mole per cent perchloric acid to 0.0106 at 100 per cent acid.

The Raman spectrum has been studied by Redlich and co-workers,³² by Fonteyne^{10, 11} and by Simon and co-workers.^{42, 44, 45} Simon concludes from spectroscopic and viscosimetric measurements that the anhydrous acid exists only in the pseudoform state. Goehler and Smith¹⁴ found that during the low pressure distillation of concentrated (73 per cent) perchloric acid, a dissociation takes place as follows:



They have prepared anhydrous perchloric acid in yields of approximately 10 per cent by this method.

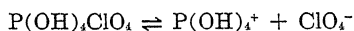
Reactions

Anhydrous perchloric acid is an extremely powerful oxidizing agent. It will cause explosions upon contact with most organic substances. Vorländer and Kaascht⁶⁷ studied several of the reactions of the anhydrous acid. They found that chlorine dioxide will turn the acid yellow to dark brown and form a mushy crystalline precipitate. The crystalline mass and supernatant brown liquid deflagrate on contact with ice water. The crystals form a yellow solution in chloroform. In dry atmosphere the crystals melt at 0°C to form a red-brown solution which loses chlorine dioxide. A dark brown solution results also from the addition of potassium chlorate to the

anhydrous acid but potassium perchlorate can be recrystallized unchanged from both the anhydrous and 70 per cent acids.

The anhydrous acid is miscible with chloroform with which it forms a safe mixture. If a drop of perchloric acid is placed on dry potassium permanganate, a yellow gas is formed, deflagration takes place and a manganese oxide is formed. Bromine is very slightly soluble in the acid without reaction. Neither hydrogen bromide nor hydrogen chloride react with the anhydrous acid. Hydrogen iodide, on the other hand, ignites on contact with the acid.² Arsenic dissolves in the anhydrous acid to give a clear yellowish solution. Thionyl chloride deflagrates on contact with the acid while sulfuryl chloride fails to react at all. Phosphorus oxychloride forms a homogeneous solution with the acid without detectable reaction while phosphorus pentachloride reacts to give chlorine heptoxide as one product. Anhydrous perchloric acid forms an addition compound with sulfur trioxide. This complex, of the formula $\text{HClO}_4 \cdot 2\text{SO}_3$, is a liquid, immiscible with HClO_4 .⁵⁵

The complex compounds $\text{P}(\text{OH})_4\text{ClO}_4$ and $\text{Se}(\text{OH})_3\text{ClO}_4$ were prepared by Arlman.¹ They are both soluble in nitromethane in which they dissociate according to the following equations:



Heats of solution in nitromethane and heats of formation are reported.

Berthelot's value of -11.1 kcal/mole for the heat of formation of the anhydrous acid is the only determination of this quantity which has been reported.³ The electrical conductivity, viscosity and surface tension of the anhydrous acid have been measured by Usanovich and co-workers,⁶⁵ and are given in Table 2.1.

THE HYDRATES OF PERCHLORIC ACID

Van Wyk^{69, 70} determined the freezing point-composition diagram of the $\text{HClO}_4\text{-H}_2\text{O}$ system from 0 to 100 per cent HClO_4 and reported six hydrates,

TABLE 2.1. PHYSICAL PROPERTIES OF ANHYDROUS PERCHLORIC ACID⁶⁵

Properties	0°C	10°C	25°C
$\chi \times 10^3$	3.619	3.885	4.083
σ	33.90	32.41	31.26
$\eta \times 10^3$	11.89	9.46	7.95
d	1.8129	1.7915	1.7722

χ = electrical conductivity ($\text{ohm}^{-1} \text{cm}^{-1}$)

σ = surface tension (dynes/cm)

d = density (g/cm^3)

η = viscosity (poises)

TABLE 2.2. HYDRATES OF PERCHLORIC ACID

Hydrate	Boiling Point	Melting Point	Weight Per Cent Acid	ΔH_f° kcal/mole
HClO ₄ (anhyd.)		-112	100.0	-11.1
HClO ₄ ·H ₂ O		+49.9	84.8	-92.1
HClO ₄ ·2H ₂ O	203°	-17.8	73.6	-162.8
2HClO ₄ ·5H ₂ O		-29.8	69.1	
HClO ₄ ·3H ₂ O				
alpha		-37	65.0	
beta		-43.2	65.0	
2HClO ₄ ·7H ₂ O		-41.4	61.5	
HClO ₄ (aq.) at in- finite dilution				-31.41

as shown in Table 2.2. His diagram is shown in Figure 2.1. Brickwedde, at the National Bureau of Standards, has studied the system for 0 to 70 per cent HClO₄.⁵ She obtained curves of the same general shape as Van Wyk's but the latter's temperatures are in many cases outside the experimental error of the work at the National Bureau of Standards. The two curves are shown in Figure 2.2. The discrepancies between the two remain largely unexplained. Since Van Wyk gave no diagram of his apparatus, used no stirrer except his thermometer, and gave no indication of having made emergent-stem corrections, it is not possible to estimate the accuracy of his temperatures. The existence of hydrates other than monohydrate are therefore not firmly established.

The monohydrate exists entirely as the oxonium salt H₃O⁺ClO₄⁻.^{4, 19, 21, 27, 32, 34, 50} The crystal structure of the compound has been determined in detail by x-ray diffraction.²⁴ The perchlorate ions are nearly perfect tetrahedra with an average Cl-O distance of 1.42Å. Proton magnetic resonance studies²⁰ reveal that the oxonium ion has a pyramidal structure similar to that of ammonia¹⁹ with H-H distance 1.58Å, O-H distance 0.98Å and O-H-O angle 110°. A careful investigation of the Raman spectrum⁵⁰ has confirmed previous work on structure and allowed calculation of the valence force constants.

Simon and Weist⁴⁵ have found that 77 per cent perchloric acid is 100 per cent aciform (H⁺ + ClO₄⁻).

The monohydrate is a very reactive crystalline compound. The fused monohydrate is reported to cause spontaneous ignition on contact with wood or paper.³⁷ The compound of dihydrate composition is a dense, rather viscous liquid boiling at 203°C at atmospheric pressure. It is mildly hygroscopic and fumes slightly in air. It has been proposed as a standard in acidimetry.⁵²

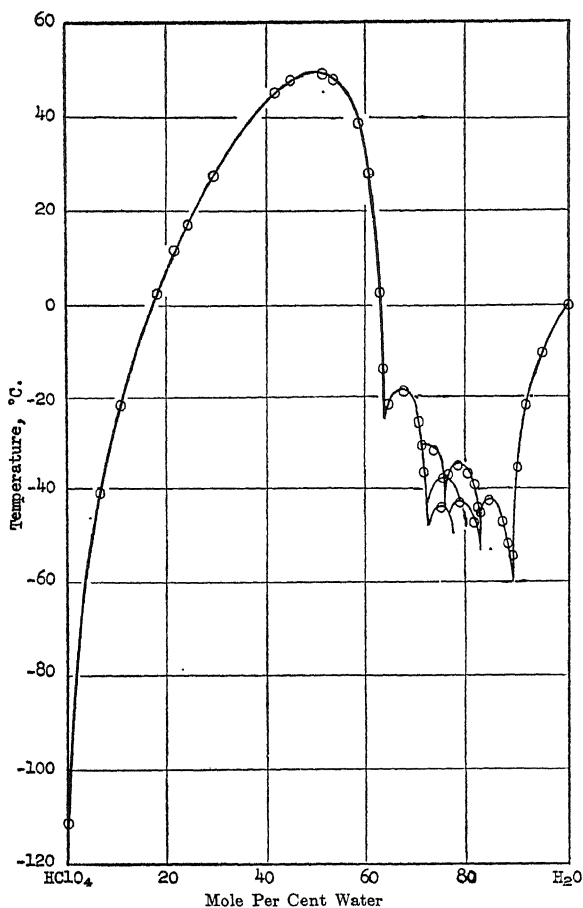


Figure 2.1. Freezing curves of perchloric acid solutions. (Wyk, H. J. Van⁷⁰)

AQUEOUS PERCHLORIC ACID

Physical Properties

Goodeve and Marsh¹⁵ measured the heat of reaction of chlorine heptoxide with excess water and calculated a value of -31.6 ± 1.7 kcal/mole for the heat of formation of aqueous perchloric acid.

The structure²⁸ and physical properties of aqueous solutions of perchloric acid have been rather extensively studied. Smith⁵¹ has used oxonium perchlorate ($\text{HClO}_4 \cdot \text{H}_2\text{O}$) as a reference standard for construction of a specific gravity-percentage composition table for strong perchloric acid solutions. He gives a table of densities of 65 to 75 per cent perchloric acid solutions at 25°C. Markham²⁵ extended the density measurements to

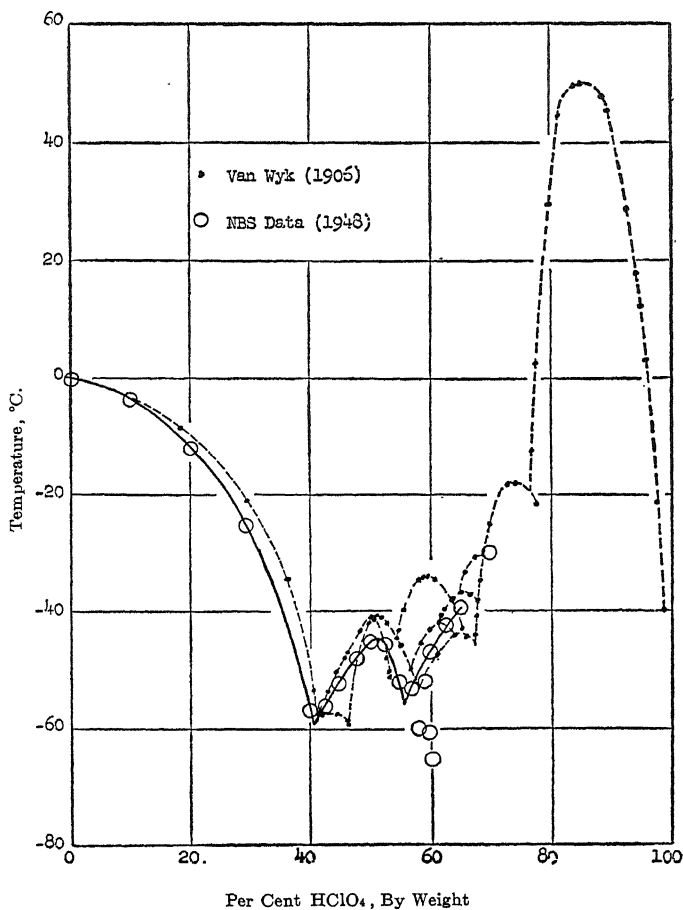


Figure 2.2. Freezing curves of perchloric acid solutions. (Brickwedde, L. H⁶)

cover the range 0 to 65 weight per cent acid. Subsequent work by Brickwedde at the Bureau of Standards⁵ has expanded the data to cover the ranges 0 to 70 per cent HClO₄ from +50 to -50°C (Table 2.3). In the same year that Brickwedde's work appeared, Clark⁶ published data covering the range from 10 to 60 weight per cent perchloric acid at temperatures from 50 to -58°C. Earlier measurements were made by Van Emster⁸ and Van Wyk.⁷⁰ The latter investigator reported densities of acids from 5 to 100 mole per cent (22.7 to 100 weight per cent). His results are given in Table 2.4 and are the only data available for acid strengths above 75 weight per cent. His values for lower concentrations differ from those of Brickwedde by 0.2 per cent.

Several studies of the viscosity of perchloric acid solutions are reported.

TABLE 2.3. DENSITIES OF AQUEOUS PERCHLORIC ACID SOLUTIONS^a

Per- centage of HClO ₄	Density at Various Temperatures (g/ml)													
	+50°C	+40°C	+30°C	+25°C	+20°C	+15°C	+10°C	0°C	-10°C	-20°C	-25°C	-30°C	-40°C	-50°C
0	0.988	0.992	0.996	0.997	0.998	0.999	1.000	1.000	—	—	—	—	—	—
5	1.015	1.020	1.024	1.026	1.027	1.028	1.029	1.031	—	—	—	—	—	—
10	1.044	1.050	1.054	1.056	1.058	1.060	1.061	1.064	(1.066) ^a	—	—	—	—	—
15	1.074	1.081	1.086	1.088	1.091	1.093	1.095	1.099	1.102	(1.105)	—	—	—	—
20	1.107	1.114	1.120	1.123	1.125	1.128	1.131	1.136	1.140	(1.144)	—	—	—	—
25	1.143	1.150 _s	1.157	1.160	1.163	1.166	1.169	1.175	1.180	(1.185 _s)	(1.189)	—	—	—
30	1.182	1.189	1.196 _s	1.200	1.204	1.207	1.210	1.217	1.223	1.228 _s	1.231	(1.233)	—	—
35	1.224	1.232	1.239 _s	1.244	1.247	1.251	1.255	1.262	1.268	1.275	1.278	(1.286)	—	—
40	1.270	1.278	1.286	1.291	1.294 _s	1.298 _s	1.303	1.311	1.318	1.326 _s	1.331	1.335	1.343	1.352
45	1.320	1.329	1.338	1.343	1.347	1.352	1.356	1.366	1.375	1.384	1.389	1.394	1.404	1.414
50	1.375	1.385	1.395	1.400	1.405	1.410	1.415	1.425	1.436	1.447	1.453	1.459	1.472	(1.484)
55	1.435	1.445	1.456 _s	1.462	1.467	1.473	1.478	1.490	1.502	1.514	1.520	1.527	1.542	1.550
60	1.499	1.510	1.521 _s	1.527 _s	1.533	1.539	1.545	1.558	1.571	1.584	1.591	1.598	1.613	1.630
65	1.567	1.578	1.590	1.596	1.603	1.609 _s	1.616	1.629	1.643	1.656	1.662	1.669	(1.682)	(1.696)
70	1.634	1.645	1.658	1.664	1.672	1.678 _s	1.685 _s	1.699	1.712 _s	1.725	1.731	1.736	—	—

^a Values in parentheses are extrapolated and may represent solutions undercooled at the temperatures indicated.

TABLE 2.4. DENSITIES OF PERCHLORIC ACID SOLUTIONS²⁰

Mole Per Cent HClO ₄	Weight Per Cent HClO ₄	Specific Gravity	
		20°C	50°C
100	100	1.7676	1.7098
92.75	98.62	1.7817	1.7259
76.15	94.69	1.8059	1.7531
63.85	90.78		1.7690
50.00	84.80		1.7756
43.4	81.06		1.7619
35.67	75.57	1.7386	1.7023
27.96	68.41	1.6471	1.6110
21.44	60.37	1.5353	1.5007
15.46	50.50	1.4078	1.3779
10.56	39.72	1.2901	1.2649
6.23	27.05	1.1778	1.1574

TABLE 2.5. ABSOLUTE VISCOSITY OF PERCHLORIC-ACID SOLUTIONS⁵
Based on Absolute Viscosity of Water at 20°C = 1.002 Centipoises

Percentage of HClO ₄ (by weight)	Absolute Viscosity (centipoises) at Various Temperatures													
	+50°C	40°C	30°C	25°C	20°C	10°C	0°C	-10°C	-20°C	-30°C	-40°C	-50°C	-60°C	
0	0.547	0.653	0.798	0.890	1.002	1.306	1.786	2.59	—	—	—	—	—	
5	.557	.662	.803	.894	1.004	1.287	1.743	2.47	—	—	—	—	—	
10	.569	.675	.813	.901	1.010	1.280	1.714	2.40	—	—	—	—	—	
15	.586	.692	.829	.913	1.022	1.286	1.701	2.347	—	—	—	—	—	
20	.610	.715	.853	.937	1.043	1.307	1.707	2.329	—	—	—	—	—	
25	.641	.750	.890	.974	1.080	1.347	1.745	2.353	—	—	—	—	—	
30	.684	.794	.940	1.031	1.139	1.413	1.815	2.434	3.415	—	—	—	—	
35	.744	.859	1.013	1.108	1.223	1.514	1.925	2.572	3.581	—	—	—	—	
40	.822	.950	1.118	1.224	1.345	1.670	2.113	2.814	3.928	5.887	9.670	18.21	—	
45	.940	1.080	1.274	1.395	1.534	1.900	2.426	3.244	4.582	7.139	11.96	23.13	—	
50	1.099	1.271	1.507	1.650	1.821	2.268	2.914	3.962	(5.732) ^a	9.084	16.22	—	—	
55	1.329	1.548	1.837	2.022	2.237	2.819	3.677	5.104	7.570	11.99	24.24	69.4	—	
60	1.646	1.928	2.296	2.532	2.813	3.560	4.713	6.700	9.962	16.25	34.70	90.9 ₅	345	
65	2.076	2.440	2.913	3.211	3.560	4.523	5.969	8.40	12.37	19.88	—	—	—	
70	2.639	3.094	3.692	4.060	4.504	5.675	7.333	9.92	14.19	22.19	—	—	—	

^a Value interpolated from curve.

Probably the most extensive is that of Brickwedde,⁵ who reports absolute and kinematic viscosities for 0 to 70 per cent perchloric acid solutions in the temperature range +50 to -60°C. These values are given in Tables 2.5 and 2.6. Clark⁶ has measured viscosities of 10 to 60 per cent perchloric acid solutions in the same temperature range and obtained results in good agree-

TABLE 2.6. KINEMATIC VISCOSITY OF PERCHLORIC-ACID SOLUTIONS^a

Percentage of HClO ₄ (by weight)	Kinematic Viscosity (centistokes) at Various Temperatures												
	+50°C	40°C	30°C	25°C	20°C	10°C	0°C	-10°C	-20°C	-30°C	-40°C	-50°C	-60°C
0	0.554	0.658	0.801	0.893	1.004	1.306	1.786	2.59	—	—	—	—	—
5	.549	.649	.784	.871	0.978	1.251	1.691	2.40	—	—	—	—	—
10	.545	.643	.771	.853	.955	1.206	1.611	2.25	—	—	—	—	—
15	.546	.640	.763	.839 _s	.937	1.174	1.548	2.130	—	—	—	—	—
20	.551	.642	.762	.834	.927	1.156	1.503	2.043	—	—	—	—	—
25	.561	.652	.769	.840	.929	1.152	1.485	1.994	—	—	—	—	—
30	.579	.668	.786	.859	.946	1.168	1.491	1.990	2.78	—	—	—	—
35	.608	.697	.817 _s	.891	.981	1.206 _s	1.525	2.028	2.809	—	—	—	—
40	.647	.743	.869	.948	1.039	1.282	1.612	2.135	2.961	4.410	7.20	13.47	—
45	.712	.813	.952	1.039	1.139	1.401	1.776	2.359	3.311	5.121	8.52	16.36	—
50	.799	.918	1.080	1.178 _s	1.296	1.603	2.045	2.759	(3.961) ^a	6.226	11.02	—	—
55	.926	1.071	1.261	1.383	1.525	1.907	2.468	3.398	5.000	7.852	15.72	44.5	—
60	1.098	1.277	1.509	1.657 _s	1.835	2.304	3.025	4.265	6.289	10.17	21.51	55.8	209
65	1.325	1.546	1.832	2.012	2.221	2.799	3.664	5.11	7.47	11.91	—	—	—
70	1.615	1.881	2.227	2.440	2.694	3.367	4.316	5.79	8.227	12.78	—	—	—

^a Value interpolated from curve.

TABLE 2.7. ABSOLUTE VISCOSITIES OF PERCHLORIC ACID SOLUTIONS

Mole Per Cent HClO ₄	Weight Per Cent HClO ₄	Absolute Viscosity (centipoises)			
		20°C		50°C	
		Van Wyk ^a	Simon ^b	Van Wyk ^a	Simon ^b
100.0	100.0	0.76		0.563	
78.5	95.3	1.884		1.187	
76.8	94.9	2.004		1.253	
65.4	91.3			1.975	
64.8	91.1			2.007	
48.6	84.1			3.457	
48.5	84.03				3.417
43.1	80.87				4.001
42.5	80.5			3.758	
38.8	77.95		7.300		4.014
36.6	76.3	6.222		3.479	
36.6	76.26		6.854		3.850
34.2	74.47		6.271		3.639
31.8	72.31		5.366		3.233
31.0	71.5	4.679		2.729	
29.8	70.28		4.811		2.909
28.1	68.56		4.251		2.519
25.0	65.1	3.417		1.991	
21.2	60.11		2.890		1.680
20.0	58.3	2.515		1.488	
14.6	48.8	1.693		1.017	
10.0	38.3	1.293		0.777	
5.0	22.7	1.052		0.618	
0.0	0.0	1.002		0.547	

^a Wyk, H. J. Van.⁷⁰^b Simon, A.⁴⁸

ment with those of Brickwedde. Viscosity measurements at higher concentrations have been made by Van Wyk.⁷⁰ Viscosities reported by Simon and Weist⁴⁵ in 1952 were later found to be in error. A recheck by Simon⁴³ produced the values given in Table 2.7 along with those of Van Wyk.

The vapor pressures and activity coefficient of aqueous perchloric acid solutions have been measured by Pearce and Nelson⁸¹ and by Robinson and Baker.⁸⁵ These investigators report activity of the solvent, activity coefficient of the ions, partial molal volumes, osmotic coefficient and free energy change accompanying the transfer of solvent and solute at 25°C. Values of osmotic and activity coefficients at a range of concentrations have been tabulated.⁸⁶

Neros and Eversole⁸⁰ have reported the surface tension of 0 to 72 per cent perchloric acid solutions at 15, 25, and 50°C. A maximum is found to exist at the composition corresponding to HClO₄·3H₂O at all temperatures. Their data at 25°C are given in Table 2.8.

TABLE 2.8. SURFACE TENSION OF PERCHLORIC ACID SOLUTIONS³⁰

Concentration of Acid (wt %)	15°C		25°C		50°C	
	d^a (g/ml)	σ	d^a (g/ml)	σ	d^a (g/ml)	σ
0.00	0.9991	73.51	0.99707	71.97 ^b	0.9881	68.16
4.86	1.0277	72.52	1.02476	71.18	1.0140	67.60
10.01	1.0598	71.66	1.05597	70.34	1.0436	66.97
20.38	1.1307	70.46	1.12534	69.21	1.1096	66.12
30.36	1.2098	69.82	1.20272	68.57	1.1827	65.66
40.37	1.3030	69.72	1.29396	68.49	1.2714	65.74
53.74	1.4565	70.33	1.44528	69.02	1.4166	66.60
60.70	1.5487	70.88	1.53579	69.69	1.5045	67.40
63.47	1.5858	70.77	1.57515	69.73	1.5416	67.44
67.59	1.6410	70.67	1.63016	69.71	1.5964	67.41
70.43	1.6790	70.07	1.66637	69.54	1.6344	67.26
72.25	1.7034	69.96	1.69495	69.01	1.6595	66.85

^a International Critical, Tables Vol. III, p. 54, New York, McGraw-Hill Book Company, Inc., 1928.

^b *Ibid.*, Vol. IV, p. 447.

The refractive index of aqueous perchloric acid solutions of 50 to 70 per cent concentrations has been reported at 20, 25, and 30°C by Smith and Lamplough.⁵³ A nomograph (Figure 2.3) has been constructed from their data by Davis.⁸

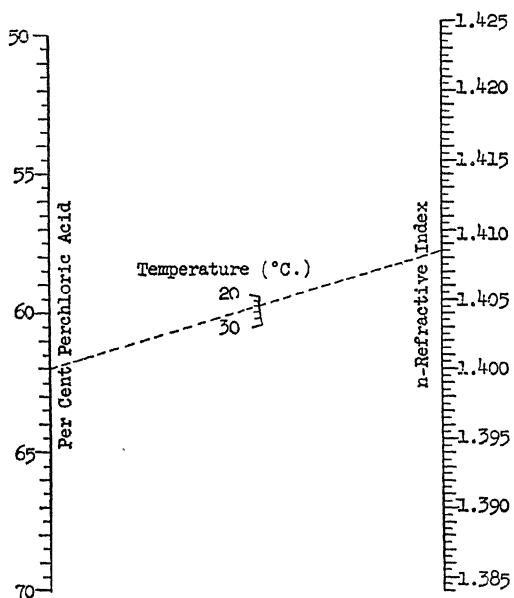


Figure 2.3. Nomograph relating perchloric acid concentration with refractive index. (Davis, D. S.⁸)

The vapor-liquid equilibrium diagram for the perchloric acid-water system has been determined by Van Wyk⁷⁰ for the concentration range from zero to the constant boiling composition of 72.4 per cent acid. He also reported boiling points at 18 mm Hg for compositions from 30 to 100 mole per cent acid.

The electrical resistivity of perchloric acid solutions of from 10 to 70 weight per cent has been measured by Brickwedde⁵ from -60 to $+50^{\circ}\text{C}$. She finds that the empirical relationship

$$\frac{\log (20 \times \text{kinematic viscosity})}{\sqrt{T} \log (4 \times \text{resistivity})} = K = 0.100$$

holds for solutions varying from 30 to 60 per cent of perchloric acid and over the temperature range -50 to $+50^{\circ}\text{C}$. In this range the average deviation is 1.8 per cent. A similar relationship was found for sulfuric acid solutions by Vinal and Craig.⁶⁶

A conductance diagram at 50°C for the complete range 0 to 100 per cent perchloric acid has been determined by Usanovich and Sumarokova.⁶² They also obtained partial curves at 20 and 60°C . By considering the conductivity curve, the temperature coefficient of conductivity, and a plot of the product (viscosity \times conductivity) *vs.* concentration, these authors conclude that the mono- and dihydrates both manifest themselves in the liquid phase.

Klochko and Kurbanov²² found discontinuities in the conductance curve of perchloric acid solutions at 25 and 20 mole per cent acid, corresponding to the tri- and tetrahydrates. A conductance maximum was found at 9.2 mole per cent acid, in close agreement with the maximum at about 10 per cent reported by Usanovich.

Other workers^{12, 13} have also made measurements of density, viscosity and electrical conductivity of perchloric acid solutions over more limited concentration ranges. The Raman spectra of perchloric acid solutions were reported by Redlich and co-workers.³²

Reactions of Aqueous Perchloric Acid

In its usual commercial form, 70 to 72 per cent aqueous solution, perchloric acid has no oxidizing power in the cold. Its properties are those of a strong acid. The hot, concentrated acid, however, is a strong oxidizing agent. This unique behavior makes it valuable in analytical work. It is useful in the wet ashing of organic matter⁴⁹ and in the determination of chromium in stainless steel.⁴⁶ The determination of chromium in chrome-tanned leather⁴⁷ utilizes the oxidizing action of hot perchloric acid to first destroy the organic matter, then oxidize the chromium to chromate. The solution is then cooled and diluted, after which chromate can be determined

TABLE 2.9. THE REACTIONS OF METALS WITH 72 PER CENT PERCHLORIC ACID³³

Metal	Products	Metal	Products
Magnesium	Mg ⁺⁺ , H ₂	Lead	Pb ⁺⁺ , H ₂ , Cl ₂ , HCl
Aluminum	Al ⁺⁺⁺ , H ₂ , Cl ⁻ (trace)	Copper	Cu ₂ ⁺⁺ , Cu ⁺⁺ , HCl
Zinc	Zn ⁺⁺ , H ₂ , Cl ⁻ (trace)	Mercury	Hg ⁺⁺ , HCl
Cadmium	Cd ⁺⁺ , H ₂ , Cl ⁻ (trace)	Arsenic	H ₃ AsO ₄ , HCl
Chromium	(1) Cr ⁺⁺⁺ , Cr ⁺⁺ (2) CrO ₄ ⁻ , HCl	Antimony	Sb ₂ O ₄ , HCl
Iron	Fe ⁺⁺⁺ , Fe ⁺⁺ , H ₂ , HCl, Cl ₂	Bismuth ^a	Bi ⁺⁺⁺ , Cl ⁻
Cobalt	Co ⁺⁺ , H ₂ , HCl	Silver	AgCl, Ag ⁺
Nickel	Ni ⁺⁺ , H ₂ , HCl	Platinum	No reaction
Tin	SnO ₂ , Cl ₂ , Cl ⁻	Gold	AuCl ₄ ⁻ (trace)

^a Explosions have been reported resulting from the reaction of bismuth with hot perchloric acid. See Chapter 4, "Metal Perchlorates."

by titration with ferrous sulfate, the cold dilute perchloric acid having no further oxidizing action.

The cold 72 per cent acid reacts with active metals with the liberation of hydrogen and formation of the perchlorates. When heated, reduction of the perchlorate ion begins to take place and hydrogen chloride becomes a product. Reedy³³ has summarized the reactions of perchloric acid with a number of metals, as shown in Table 2.9. Marked passivity is noted in certain cases: e.g., iron, chromium, nickel, etc.

The various reactions of perchloric acid may be simply explained in terms of concurrent ionic and molecular reactions. The ionized form acts as a strong acid and exhibits the reactions of the hydrogen ion. At elevated temperatures, however, the oxidizing action of molecular perchloric acid becomes more pronounced, accounting for the observed distribution of products.

The lack of oxidizing power of cold perchloric acid permits the preparation of numerous organic salts of the acid. Many amine perchlorates have been reported, as have perchlorate esters. These compounds are discussed in more detail in Chapter 5.

A series of graphite salts of perchloric acid has been reported by Rüdorff and Hofmann.³⁹ These can be prepared by the reversible interchange of perchloric acid with sulfuric acid in the corresponding sulfuric acid salts. Crystal structures of these compounds were reported by Rüdorff.³⁸

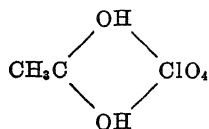
Sakurada and Okamura,⁴⁰ in a study of molecular compounds of cellulose, determined the composition of perchloric acid-cellulose to be 2C₆H₁₀O₅ · HClO₄ · 2H₂O.

OTHER SYSTEMS CONTAINING PERCHLORIC ACID

Perchloric acid has found extensive use in mixtures with acetic acid in electropolishing baths. For this reason several studies have been made of

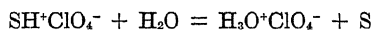
the system perchloric acid-acetic acid-water. Those concerned with explosive mixtures are discussed in Chapter 11.

Jolly¹⁷ determined the entropy of ionization of acetic acid by measuring the heat of neutralization of sodium acetate with perchloric acid in acetic acid solution. The determination was based on the assumption that perchloric acid is completely ionized in anhydrous acetic acid. The basis for this assumption was a determination of the dissociation by Kolthoff and Willman,²³ using conductance measurements. These authors stated that perchloric acid behaves like a strong electrolyte in acetic acid. It is present partly as ions and partly as ion pairs



Their measurements showed that the equivalent conductance falls off rapidly with increasing concentration and increases relatively slowly upon addition of water. Perchloric acid was much stronger than hydrobromic, sulfuric, hydrochloric or nitric acids, which decreased in strength in that order.

Kahane, in 1948, made calorimetric measurements on the heat of mixing of $\text{HClO}_4 \cdot 2.5\text{H}_2\text{O}$ and acetic anhydride in glacial acetic acid.¹⁸ He found that the heat of mixing, 20 kcal/mole, was that expected from the formation of anhydrous perchloric and acetic acids. The Hammett acidity function, H_0 , was determined by Smith and Elliott⁵⁴ for dilute solutions of several strong acids in glacial acetic acid, using indicators α -naphtholbenzein and *o*-nitroaniline. Using the conductance data of Kolthoff and Willman, they calculated 9×10^{-7} for the dissociation constant for perchloric acid in glacial acetic acid. This was interpreted as representing dissociation of the ion pair. Addition of water to the solution sets up the following equilibrium



where S represents an acetic acid molecule. Both ion pairs would be expected to dissociate to approximately the same extent. Thus, addition of water to a perchloric-acetic acid mixture results in only a small change in the total concentration of ions.

The considerable number of explosions which have been observed in cold perchloric-acetic acid mixtures indicate that any dissociation taking place in these mixtures is much different from that in water solutions of perchloric acid.

The conductivity, viscosity and density of the systems formed by perchloric acid with acetic acid, monochloroacetic acid and dichloroacetic acid

have been studied by Sumarokova and Usanovich,^{57, 58, 63, 64} and the system perchloric acid-trichloroacetic acid by Sumarokova and co-workers.^{56, 57}

The System Perchloric Acid-Acetic Acid (Ref. 64)

Measurements were made at 20, 35, and 50°C. The viscosity-concentration curves at all temperatures studied have maxima at 32.54 mole per cent perchloric acid. The conductivity-concentration curves at all three temperatures rise sharply from pure perchloric acid to a maximum at 82.95 mole per cent HClO_4 , then drop to a minimum at 32.54 mole per cent, rise to a slight maximum at 12.14 mole per cent, and then drop to the low conductance of pure acetic acid. Density decreases steadily from pure perchloric acid to pure acetic acid, values at 20°C being: perchloric acid, 1.7716; 51.17 mole per cent perchloric acid, 1.5746; 4.65 mole per cent perchloric acid, 1.1176.

The System Perchloric Acid-Monochloroacetic Acid (Ref. 63)

Viscosity-concentration curves show a maximum at a concentration of about 32.7 mole per cent perchloric acid at 35 and 50°C, but crystallization of monochloroacetic acid prevented observation of a maximum at 20°C. Values of maximum viscosity at 35 and 50°C are 5.881 and 2.441 centipoises. The conductivity curves show maxima at about 80 mole per cent perchloric acid. The maximum conductivities at 20, 35, and 50°C are 0.05261, 0.06360 and 0.07778 $\text{ohm}^{-1} \text{cm}^{-1}$, respectively. The conductivity of perchloric acid is given as 0.00250 $\text{ohm}^{-1} \text{cm}^{-1}$ and that of acetic acid is less than 0.001 $\text{ohm}^{-1} \text{cm}^{-1}$.

The curve of $1/d$ against concentration is convex toward the concentration axis. At 20°C it rises from 0.57 for 100 weight per cent perchloric acid to 0.66 for 20 weight per cent perchloric acid.

The System Perchloric Acid-Dichloroacetic Acid (Ref. 58)

The viscosity-concentration curves for this system are S-shaped. The reported viscosity values for perchloric acid and for dichloroacetic acid at 20°C are 0.460 and 4.20; at 35°, 0.39 and 2.60; and at 50°, 0.32 and 1.79 centipoises. These viscosity values for HClO_4 are considerably less than those reported by Van Wyk (Table 2.7). The conductance-concentration curves give rise to rather sharp maxima at a concentration of 79.5 mole per cent perchloric acid, and values of maximum conductance at 20, 35 and 50°C being 0.02587, 0.02620 and 0.02618 $\text{ohm}^{-1} \text{cm}^{-1}$. The curve of $1/d$ against concentration is slightly S-shaped. Values given for the density of perchloric acid and dichloroacetic acid at 20° are 1.778 and 1.526 g/cc.

TABLE 2.10. PROPERTIES OF PERCHLORIC ACID-TRICHLOROACETIC ACID MIXTURES⁵⁶

Properties	Mole Per Cent HClO ₄		
	79.7	54.6	23.7
Viscosity, millipoises	7.93	15.11	28.36
Conductance, κ	0.00566	0.00125	0.00098
$d\kappa/dT$, %	0.79	4.45	11.48
Density	1.6560	1.6533	1.6177

The System Perchloric Acid-Trichloroacetic Acid (Ref. 56)

The viscosity curves in this system are convex toward the composition axis and rise continuously from perchloric acid to trichloroacetic acid. The decrease of viscosity at higher temperatures is more pronounced at higher trichloroacetic acid concentrations. Conductance curves have a similar shape but fall uniformly and rapidly from perchloric acid to trichloroacetic acid. The temperature coefficient of the electrical conductance between 50 and 60°C rises rapidly from perchloric acid to trichloroacetic acid. A plot of the product of conductance and viscosity falls almost linearly (with a slight convexity to the composition axis) from perchloric acid to trichloroacetic acid. The specific volume ($1/d$) rises from perchloric acid to trichloroacetic acid along a curve concave to the composition axis. Examples of the data at 60°C are tabulated in Table 2.10.

From consideration of the curves for viscosity, conductance, temperature coefficient of conductance and the product of viscosity and conductance as a function of concentration, Sumarokova and Grushkin⁵⁶ claim to have detected the following compounds: $\text{CH}_2\text{ClCOOH} \cdot 2\text{HClO}_4$, $\text{CHCl}_2\text{COOH} \cdot \text{HClO}_4$, $\text{CHCl}_2\text{COOH} \cdot 2\text{HClO}_4$ and $2\text{CH}_3\text{COOH} \cdot \text{HClO}_4$. None of the above compounds were isolated, however.

Viscosity diagrams have been discussed by Udovenko⁶⁰ and by Usanovich.⁶¹ These workers feel that both maxima and inflection points in viscosity diagrams can be best explained by relative dissociation or interaction of compound with solvent. Thus the observed maximum in the acetic acid-perchloric acid viscosity curve could be due to interaction of the compound $\text{CH}_3\text{COOH} \cdot \text{HClO}_4$ with acetic acid. Similarly, the S-shaped viscosity curve found in the perchloric acid-dichloroacetic acid system could be the result of a greater degree of association in dichloroacetic acid than in the compound formed between the two.

The equimolar compound $\text{CH}_3\text{COOH} \cdot \text{HClO}_4$ was obtained by Hantzsch and Langbein in the crystalline form.¹⁶ This compound has a melting point of 41°C.

TABLE 2.11. DISSOCIATION CONSTANTS OR CONDUCTIVITIES OF SOLUTIONS OF PERCHLORIC ACID IN VARIOUS SOLVENTS

Solvent	-Log K	Δ_0
Formic acid ^a	0.28 (Quinhydrone electrode) 0.56 (glass electrode)	
Pyridine ^b	3.23	
Methanol ^c	Strong electrolyte	
Ethanol ^c	Strong electrolyte	
Acetone ^c	Strong electrolyte	
Nitromethane ^d		127
Nitrobenzene ^e		43

^a Shkodin, A. M., Izmailov, N. A., and Dzyuba, N. P.⁴¹^b Davies, Mansel M.⁷^c Murray-Rust, D. M. and Hartley, Harold.²⁹^d Wright, C. P., Murray-Rust, D. M., and Hartley, Harold.⁵⁸^e Murray-Rust, D. M., Hadow, H. J. and Hartley, Harold.²⁸

The System Perchloric Acid-Sulfuric Acid

Usanovich, Sumarokova and Udovenko⁶⁵ determined simultaneously the conductivity, viscosity and surface tension of perchloric acid-sulfuric acid mixtures. The viscosity curves at 0, 10 and 25°C rise slowly from pure perchloric acid to 50 mole per cent sulfuric acid, then rapidly to pure sulfuric acid. The conductivity curves pass through a maximum at about 33 mole per cent sulfuric acid. The surface tension curves are very slightly concave and obey fairly well the Whatmough equation $\sigma_{add} = [\sigma_x X + (1 - X)\sigma_y]R$, where X is the mole fraction of H_2SO_4 and R is a correction factor calculated from the density curve. It is concluded that the two components of the system do not interact.

Dissociation In Some Nonaqueous Solvents

The dissociation constants or conductances of solutions of perchloric acid in a number of solvents have been measured. Some values are shown in Table 2.11.

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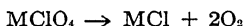
3. ALKALI METAL, AMMONIUM AND ALKALINE EARTH PERCHLORATES

AMMONIUM AND ALKALI METAL PERCHLORATES

The perchlorates of the Group I elements and ammonium perchlorate are white, crystalline solids. Thermochemical constants for these compounds are summarized in Table 3.1. All of the compounds except lithium perchlorate are dimorphic, exhibiting transitions from rhombic to cubic forms at the temperatures shown in Table 3.2. Crystal structures and magnetic susceptibilities are reported by Mellor.¹ Lithium perchlorate alone has a well-defined melting point. The others decompose upon melting or within a very short temperature range of the melting point.

Thermochemical data for the alkali metal perchlorates in solution are given in Table 3.3.

The heats of formation of the metal perchlorates are very nearly the same as the heats of formation of the corresponding chlorides. The reaction:



thus takes place with little net energy change. For this reason perchlorates, especially those of the light metals, are highly favored as solid oxidizers for rocket propellants. The oxygen content of the alkali metal perchlorates is given in Table 3.4. The oxygen in ammonium perchlorate is not all available for combustion of a fuel, however. Some must be used to burn the ammonium ion.

Marvin and Woolaver⁴⁷ studied the thermal decomposition of lithium, sodium and potassium perchlorates, among others, by means of the thermo-balance. Their results verify that the decomposition yields the chloride and oxygen only in these three cases. Curves of weight loss *vs.* temperature for these compounds show a sharp break where decomposition begins, followed by a nearly isothermal region of decreasing weight.

Perchlorates are unusually soluble in organic solvents. Table 3.5 lists the solubilities of a number of perchlorates in a variety of solvents. Data for the first eight solvents were obtained by Willard and Smith.⁹² The last three, for sodium and potassium perchlorates only, were measured by Isbin and Kobe.³⁵ The low solubility of potassium perchlorate in ethanol is the basis of one method for its analytical determination.

Molar, cationic and anionic magnetic susceptibilities have been determined for the Group I perchlorates⁵⁶ with the results shown in Table 3.6.

TABLE 3.1. THERMOCHEMICAL DATA FOR THE AMMONIUM AND ALKALI METAL PERCHLORATES

	ΔH_f° ₂₉₈	ΔF_f° ₂₉₈	S_f° ₂₉₈	C_p°	Solubility ^a g/100 g H ₂ O at 25° C	Density
NH ₄ ClO ₄	-69.42				24.922	1.952
LiClO ₄	-91.77				59.71	2.429
NaClO ₄	-92.18				209.6	2.5357 ^b
KClO ₄	-103.6	-72.7	36.1	26.33	2.062	2.5298
RbClO ₄	-103.87	-73.19	38.4		1.338	2.9
CsClO ₄	-103.86	-73.28	41.89	25.71	2.000	3.327

^a Willard, H. H. and Smith, G. F.⁹²^b Fernández Alonso, J. I. and Gascó, L.⁹⁴

TABLE 3.2. PHASE TRANSITION IN ALKALI METAL PERCHLORATES

Compound	Temp.	Transition
NH ₄ ClO ₄	240 ^{a, b}	Rhombic-cubic
LiClO ₄	247 ^c	Solid-liquid
NaClO ₄	313 ^a , 308 ^b	Rhombic-cubic
KClO ₄	300 ^b	Rhombic-cubic
RbClO ₄	281 ^a , 279 ^b	Rhombic-cubic
CsClO ₄	224 ^a , 219 ^b	Rhombic-cubic

^a Gordon, Saul and Campbell, Clement.²⁷^b Vorländer, D. and Kaascht, E.⁸⁸^c Markowitz, M. M.⁴⁶

The electrical conductances at 25°C of aqueous solutions of lithium, sodium and potassium perchlorates were reported by Jones,³⁷ who calculated the limiting conductance of perchlorate ion to be 67.32 ± 0.06 conductance units. From measurements of the indices of refraction of solutions of perchloric acid and sodium and ammonium perchlorate, Mazzucchelli and Vercillo⁵³ deduced 6.66 ± 0.06 as the difference in molar refractive power between perchlorate ion and chloride ion. Mathias and Filho⁴⁸ measured the molar refractions of lithium and sodium chlorates and perchlorates and found that the molar refractions of chlorate and perchlorate ions as experimentally determined for various concentrations agree with the values predicted theoretically from the polarization of the electron pair and the oxygen ions in relation to positive centers of various field intensity.

Ammonium Perchlorate

Ammonium perchlorate is a colorless, crystalline compound with a density of 1.95 g/cc. The refractive indices of the crystal are 1.4824, 1.4828 and 1.4868.⁹⁴ The molar refraction is 17.22. It is prepared by a double displacement reaction between sodium perchlorate and ammonium chlo-

TABLE 3.3. THERMOCHEMICAL DATA FOR THE ALKALI METAL PERCHLORATES IN SOLUTION⁶⁷

Compound	State	$\Delta H_f^\circ_{298}$	$\Delta F_f^\circ_{298}$	S°_{298}
NH_4ClO_4	in 500 H_2O	-63.2		
	∞ H_2O	-63.15		
NaClO_4	std. state, hyp. m = 1	-88.69	-65.16	57.9
	in 400 H_2O	-88.76		
	600	-88.73		
	1,000	-88.70		
	2,000	-88.68		
	5,000	-88.67		
	∞	-88.69		
	in CH_3OH	-94.6		
	in $\text{C}_2\text{H}_5\text{OH}$	-92.6		
KClO_4	std. state, hyp. m = 1	-91.45	-70.04	68.0
	in 500 H_2O	-91.580		
	600	-91.549		
	700	-91.532		
	800	-91.518		
	900	-91.507		
	1,000	-91.499		
	1,500	-91.474		
	2,000	-91.461		
	3,000	-91.447		
	4,000	-91.441		
	5,000	-91.437		
	8,000	-91.433		
	10,000	-91.433		
	20,000	-91.434		
	50,000	-91.438		
	100,000	-91.442		
	200,000	-91.444		
	500,000	-91.446		
	∞	-91.45		
RbClO_4	std. state, hyp. m = 1	-90.3	-70.02	73.2
CsClO_4	std. state, hyp. m = 1	-90.6	-69.98	75.3

TABLE 3.4. OXYGEN CONTENT OF THE ALKALI METAL PERCHLORATES

Compound	Weight Per Cent Oxygen
NH_4ClO_4	54.5
LiClO_4	60.1
NaClO_4	52.2
KClO_4	46.1
RbClO_4	34.6
CsClO_4	27.5

TABLE 3.5. SOLUBILITIES OF PERCHLORATES IN ORGANIC SOLVENTS, g/100 g SOLVENT AT 25°C^{35, 32}

Cation	Solvent										
	Methyl Alcohol	Ethyl Alcohol	n-Propyl Alcohol	n-Butyl Alcohol	i-Butyl Alcohol	Acetone	Ethyl Acetate	Ethyl Ether	Ethylene-diamine	Monochloramine	Ethylene Glycol
Ammonium	6.862	1.907	0.3865	0.0170	0.1272	2.260	0.032	Insol.			
Lithium	182.25	151.76	105.00	79.31	58.05	136.52	95.12	113.72			
Sodium	51.355	14.705	4.888	1.864	0.786	51.745	9.649	Insol.	30.1	90.8	75.5
Potassium	0.1051	0.012	0.010	0.0045	0.0050	0.1552	0.0015	Insol.	2.81	1.36	1.03
Rubidium	0.060	0.009	0.006	0.002	0.004	0.095	0.016	Insol.			
Cesium	0.093	0.011	0.006	0.006	0.007	0.150	Insol.	Insol.			

TABLE 3.6. MAGNETIC SUSCEPTIBILITIES OF GROUP I PERCHLORATES ($\times 10^6$)⁵⁶

Salt	Molar	Cationic	Anionic
NH ₄ ClO ₄	46.3	18.0	28.3
LiClO ₄	32.8	4.2	28.7
NaClO ₄	37.6	9.2	28.4
KClO ₄	47.4	18.5	28.9
CsClO ₄	69.9	41.0	28.9

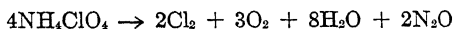
TABLE 3.7. THE SYSTEM H₂O-NH₄ClO₄²³

Solid Phase	Temp. (°C)	Composition of Solution in Grams per 100 Grams	
		NH ₄ ClO ₄	H ₂ O
NH ₄ ClO ₄	0	10.74	89.26
NH ₄ ClO ₄	25	20.02	79.98
NH ₄ ClO ₄	45	28.02	71.98
NH ₄ ClO ₄	60	33.64	66.36
NH ₄ ClO ₄	75	39.45	60.55
NH ₄ ClO ₄ + Ice	-2.7	9.8	90.2

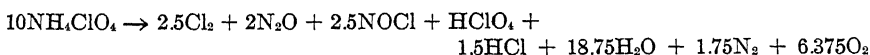
ride⁷² and crystallizes from water as the anhydrous salt. Phase relationships in the sodium chloride-ammonium perchlorate-water system are illustrated in this last reference. The salt has no known hydrates but forms a triammine which is unstable at room temperature.⁷⁹ Its solubility in liquid ammonia is 137.93 g/100 g NH₃ at 25°C.³⁴ The water solubility of ammonium perchlorate as determined by Freeth²³ is given in Table 3.7.

This reference contains complete data on ternary and quaternary equilibria in the system sodium perchlorate-ammonium sulfate-ammonium perchlorate-sodium sulfate-water at 60 and 25°C. A diagram of the reciprocal salt pairs at two temperatures is shown in Figure 3.1.

In view of the use of ammonium perchlorate as an oxidizer in rocket propellants, its thermal decomposition has been of considerable interest and has been studied extensively by Bircumshaw and coworkers.^{7, 8, 10} He found that below 300°C the equation



represented the major part of the products. Above 300°C the proportion of nitric oxide became appreciable and increasing, and above 350°C the equation⁵⁵



agrees well with the gas analysis. The nitric oxide reacts with the chlorine so that it was analyzed as nitrosyl chloride.

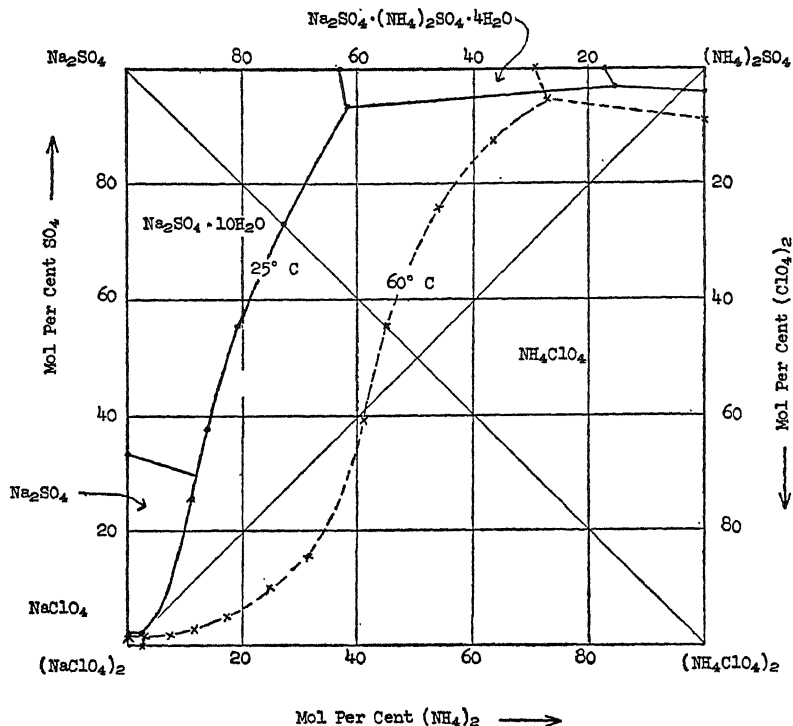


Figure 3.1. Jänecke diagram of reciprocal salt pair system. $\text{Na}_2\text{SO}_4 - \text{NH}_4\text{ClO}_4 - \text{NaClO}_4 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$ at 25° and 60°C. (Freeth, F. A. ²³)

It was found that below 290°C only 28 to 30 per cent of the salt decomposed, the residue being primarily undecomposed ammonium perchlorate. Exposure of this residue to water vapor "rejuvenated" it and upon further heating the decomposition would resume. Various other solvents were studied and the "rejuvenating" action was found to be proportional to the extent of solubility of the perchlorate in the solvent at 25°C.

Three separate activation energies have been observed for ammonium perchlorate decomposition. An activation energy of 29.6 kcal/mole was observed below 240°C, and 18.9 kcal/mole above 240°. This change coincides with the crystal transition from orthorhombic to cubic (see Table 3.2). In the 400 to 440°C temperature range the activation energy is 73.4 kcal/mole. At these higher temperatures sublimation is more rapid than is the solid phase decomposition and the large activation energy represents decomposition in the vapor phase. A region of poor reproducibility observed from 300 to 380°C is thought to be caused by the disruption of the crystal

surface by evaporation, breaking the reaction chains of the solid decomposition.

Gillespie²⁶ has made cryoscopic measurements on ammonium perchlorate in sulfuric acid and found an approximately threefold depression of the freezing point. He proposed that the reaction which takes place on dissolution can be represented as follows:



The solutions were observed to fume in ordinary air, presumably due to the escape of free perchloric acid.

The density of solutions of ammonium perchlorate in water⁵⁰ and in aqueous perchloric acid⁵¹ have been measured at 15 and 25°C. The conductivities of solutions of ammonium perchlorate in anhydrous hydrocyanic acid¹⁴ and nitromethane⁹³ show agreement with the Debye-Hückel-Onsager equation. The dissociation constant of ammonium perchlorate in liquid ammonia solution²⁸ is 5.4×10^{-3} .

The Alkali Metal Perchlorates

Some confusion exists in the literature as to whether or not the alkali metal perchlorates possess well-defined melting points. Some handbooks^{32, 42} list melting points for sodium and potassium perchlorates but not for the rubidium and cesium salts. Gordon and Campbell²⁷ listed melting points for all of the alkali metal perchlorates, obtained from an extensive differential thermal analysis study. This technique measures only heat effects, however, and the phenomena causing the effects must be determined by auxiliary observations. A thermogravimetric study by Marvin and Woolaver⁴⁷ revealed sharp breaks in the temperature-weight curves for sodium and potassium perchlorates at temperatures that correspond closely to the reported melting points. It is most probable therefore, that the liquids present at the observed melting points are eutectic compositions of the perchlorates and their decomposition products.

Lithium perchlorate melts at 247°C and does not begin to show an appreciable decomposition rate until the temperature is raised to over 400°C. This salt alone of the alkali metal perchlorates can thus be said to possess a well-defined melting point.

The trihydrate is the most common form of lithium perchlorate. The molar heat of hydration⁷⁸ is 14.2 kcal/mole and the water of hydration is extremely difficult to remove. Berglund and Sillen⁵ found that some hydrate remained in a sample held at 300°C for 12 hours. Smeets⁷⁹ has identified three ammines of lithium perchlorate containing 2, 3, and 5 molecules of ammonia per molecule of salt.

Precise studies of the crystal structure of lithium perchlorate tri-

hydrate and the anhydrous lithium and potassium salts are reported.⁶¹ From this work the precise geometry of the perchlorate ion was determined. Conductances and viscosities of some moderately concentrated solutions of lithium perchlorate in methanol-acetone at low temperatures were measured by Sears and co-workers.⁷³ Simmons and Rapp⁷⁶ measured the solubility of lithium perchlorate in water over the temperature range 0 to 172°C and the densities of the saturated solutions from 0 to 40°C. Densities of unsaturated solutions are reported by Mazzucchelli and Rossi.⁵²

The solubility of lithium and silver perchlorates in a number of organic solvents and the spectra of acetone solutions of these salts have been reported by Pullin and Pollock.⁶⁰ Several of the absorption bands of acetone are observed to be split into two components in these solutions, and from the relative intensities of these components it is concluded that complexes of the type $\text{Li}^+(\text{acetone})_2$ or $\text{Ag}^+(\text{acetone})_2$ are present in solution. Diffusion coefficients³⁰ of lithium and potassium perchlorates and osmotic and activity coefficients^{38, 65} of lithium and sodium perchlorates have been measured at 25°C.

Cryoscopic and conductivity measurements have been made on dilute solutions of lithium perchlorate in cyclohexanol,⁴¹ which show the salt to be a strong electrolyte in this solvent. The conductivities of lithium and sodium perchlorate in methanol¹⁶ and ethanol¹⁷ have been measured by Copley and co-workers, and in ethanol and acetone by Koch and Frivold.⁴¹ Walden and Hilgert⁸⁹ have reported conductivity values for lithium, sodium and potassium perchlorates in hydrazine while Coates and Taylor¹³ studied these same salts in hydrocyanic acid. Wright, *et al.*⁹³ studied numerous perchlorates in nitromethane solution including the salts of ammonium, lithium and sodium. He found that plots of conductance against the square root of concentration show pronounced curvature in the region of low concentration, making extrapolation to infinite dilution very uncertain. The effect of lithium perchlorate on the mutual solubilities of water and *n*-butyl alcohol has been reported by Durand-Gasselin and Duclaux.²¹

Sodium perchlorate forms a tetrammine⁷⁹ and a monohydrate with a heat of hydration of 2.01 kcal/mole.⁷⁸

Aqueous solutions of sodium perchlorate were studied extensively by Mazzucchelli and Pro⁵¹ who also studied solutions of the salt in perchloric acid solutions and reported solubilities and apparent specific volumes of the salts. The system water-sodium perchlorate-sodium chloride was reported by Cornec and Dickely.¹⁸ Osmotic and activity coefficients of sodium perchlorate solutions have been measured by Robinson and Stokes.⁶⁵ The Raman spectra of aqueous solutions have been reported.⁶³

Refractometric measurements⁹⁴ showed the refractive indices of the crystal to be 1.4606, 1.4617 and 1.4731, and the molar refraction 13.58.

The electrical conductivity, dissociation and temperature coefficient of conductance from 0 to 65°C of aqueous solutions of sodium perchlorate were measured by Jones.³⁶ Liquid-junction potentials and the constancy of activity factors in sodium perchlorate-perchloric acid solutions were studied by Biedermann and Sillen.⁶

The aqueous mutual system from the perchlorate and nitrate salts of ammonia and sodium were studied by Karnaukhov,³⁹ as were the triple systems entering into this system: sodium nitrate-ammonium nitrate-water; ammonium nitrate-sodium perchlorate-water; sodium nitrate-sodium perchlorate-water; and sodium perchlorate-ammonium perchlorate-water. The solid phases separating from these systems were characterized and were found to include, among others, the compound $7\text{NH}_4\text{ClO}_4 \cdot \text{NaClO}_4$ and several solid solutions. The isotherm of solubility of the system sodium perchlorate-ammonium perchlorate-water at 25°C is characterized by separation of three solid phases: NH_4ClO_4 , solid solutions of $7\text{NH}_4\text{ClO}_4 \cdot \text{NaClO}_4$ in NaClO_4 and $\text{NaClO}_4 \cdot \text{H}_2\text{O}$.

The conductivity of the salt has been measured in methanol,¹⁶ ethanol,¹⁷ hydrazine,⁸⁹ hydrocyanic acid,¹³ nitromethane⁹² and dimethylformamide.⁷³

An eutectic, melting at 310°C, in the system sodium perchlorate-barium perchlorate occurs at 43 mole per cent barium perchlorate.⁹⁶

The use of a sodium perchlorate-acetyl chloride mixture in acetic anhydride has been found to be effective in the ring acetylation of phenol ethers.⁴⁹

The refractive indices⁹⁴ of the potassium perchlorate crystal are 1.4717, 1.4724 and 1.476. The molar refraction is 15.37. Jones³⁶ measured the electrical conductivity, dissociation and temperature coefficient of conductance of aqueous solutions from 0 to 65°C. Activity coefficients were reported by Deno and Perizzolo.¹⁹ Conductances of potassium perchlorate have been measured in dimethylformamide,⁷³ hydrogen cyanide¹³ and hydrazine.⁸⁹

Potassium perchlorate forms neither hydrates nor ammoniates. Solubility data⁴ have been determined up to a temperature of 265°C. The system potassium chloride-potassium perchlorate-water has been studied at 150, 175, 200, 225 and 250°C and polytherms determined.³ Solubilities in various salt solutions were determined by Bozorth.¹¹ The system potassium perchlorate-potassium fluoborate-water was studied by Ray and Mitra.⁶²

Because of its high oxygen content and its inability to form hydrates, potassium perchlorate has found considerable use as an oxidizer in solid rocket propellants. Probably as an outgrowth of this use, the thermal decomposition of the salt has been studied quite extensively.

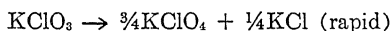
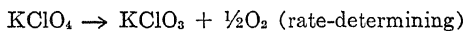
Simchen and co-workers⁷⁵ found that pure potassium perchlorate begins to decompose at 580°C. Bircumshaw and Phillips⁹ studied the decomposi-

tion quite extensively and observed a weight loss at temperatures as low as 530°C. The reaction appeared to be quite complex and the reproducibility of the results was poor. Potassium chlorate and chloride were both produced during the decomposition, and it is likely that melting is associated with the formation of a eutectic mixture of reactant and products.

The kinetics of the isothermal decomposition of potassium perchlorate under its own evolved oxygen pressure was studied in a constant volume system by Harvey and co-workers.³¹ They determined a phase diagram for the system potassium perchlorate-potassium chloride-potassium chlorate. By correlating kinetic data in the range 556 to 582°C, it was found that the decomposition proceeds by two first-order reactions. There is a solid-phase decomposition prior to the appearance of a liquid phase, and a liquid-phase decomposition which occurs after the melting of the sample is complete. The respective rates of these reactions are dependent upon the concentration of potassium perchlorate. The kinetic quantities found in this study are tabulated below:

Phase	E_a Kcal/Mole	A (Frequency Factor)	ΔS^\ddagger Cal/Mole-Deg
Solid	70.5 ± 0.4	2.36×10^{13}	0.6
Liquid	70.5 ± 0.4	1.31×10^{15}	8.6

A study of the isothermal decomposition of potassium perchlorate under constant oxygen pressure was made by Rodgers and Wassink.⁶⁶ These workers found that the rate is independent of oxygen pressure and first order in perchlorate in both solid and liquid phases. They proposed the following mechanism:



The kinetic constants are listed below:

Phase	E_a Kcal/Mole	A (Frequency Factor)	ΔS^\ddagger Cal/Mole-Deg
Solid	98.4 ± 10.5	1.8×10^{21}	36.6 ± 14.2
Liquid	80.7 ± 4.3	6.8×10^{17}	21.0 ± 5.8

The solid phase rate constants obtained in these two studies are equal at about 495°C, while the liquid phase constants are the same at about 543°C. The system is a difficult one to study and considerable scatter is observed in the experimental results.

The oxidation of carbon black by potassium perchlorate proceeds smoothly in the temperature range 320 to 385°C.⁵⁷ The reaction appears first order in each of the reactants with an activation energy of 40 ± 4 kcal. It is interesting that the activation energy is much lower than that for the decomposition of the perchlorate alone. Inhibition by potassium chloride is observed in the reaction with carbon black. Two rate equations

were found: one for the early, noninhibited portion of the reaction, and a second that holds in the later stages when the influence of potassium chloride becomes appreciable.

Extension of these studies to the reaction between potassium perchlorate and different forms of carbon³³ has revealed that the reaction is more complex than appeared previously. An empirical rate expression involving $\frac{1}{3}$ powers is given. No theoretical explanation is given for the observed rate expression.

Aromatization of cyclic hydrocarbons by solid potassium perchlorate at temperatures in the range 350 to 380°C has been reported by Patai and Rajbenbach.⁵⁸ Excellent yields of naphthalene were obtained from tetralin by this method. Benzene, phenol and *m*-cresol were also obtained from, respectively, cyclohexene, cyclohexanol or cyclohexanone and 3-methylcyclohexanone, although in much poorer yields.

ALKALINE EARTH PERCHLORATES

Anhydrous perchlorates of the alkaline earth metals can be prepared by heating ammonium perchlorate with the corresponding oxides or carbonates.⁸⁴ Reaction takes place more rapidly and at lower temperature the more basic the metal.

Very little information has been reported about beryllium perchlorate. It has been prepared by the above method but no data concerning its physical or chemical properties have appeared in the literature.

Very little thermodynamic data has been published on the alkaline earth perchlorates. Heats of formation are reported for $\text{Mg}(\text{ClO}_4)_2$ and $\text{Ba}(\text{ClO}_4)_2$ ⁶⁷ and estimated from heats of solution⁷⁸ and ionic heats of formation for $\text{Ca}(\text{ClO}_4)_2$ and $\text{Sr}(\text{ClO}_4)_2$. These values are given in Table 3.8.

None of the alkaline earth perchlorates have well-established melting points in the anhydrous state.

Endotherms were observed in a differential thermal analysis study²⁷ of magnesium and calcium perchlorate hydrates which may be associated with fusion or hydrate dissolution. Thermobalance studies⁴⁷ reveal that calcium perchlorate decomposes to calcium chloride in the same manner as the alkali metal perchlorates. Magnesium perchlorate hexahydrate, on the other hand, shows a gradual weight loss with no sharp break in the

TABLE 3.8. HEATS OF FORMATION OF THE ALKALINE EARTH PERCHLORATES

Compound	ΔH°_f ²⁹⁸	Compound	ΔH°_f ²⁹⁸
$\text{Mg}(\text{ClO}_4)_2$	-140.6	$\text{Sr}(\text{ClO}_4)_2$	-184 (est.)
$\text{Ca}(\text{ClO}_4)_2$	-178 (est.)	$\text{Ba}(\text{ClO}_4)_2$	-192.8

TABLE 3.9. SOLUBILITIES OF THE ALKALINE EARTH PERCHLORATES IN ORGANIC SOLVENTS, GRAMS PER 100 GRAMS SOLVENT AT 25°C⁹²

Cation	Water	Methyl Alcohol	Ethyl Alcohol	n-Propyl Alcohol	n-Butyl Alcohol	i-Butyl Alcohol	Acetone	Ethyl Acetate	Ethyl Ether
Magnesium	99.601	51.838	23.962	73.400	64.366	45.497	42.888	70.911	0.2908
Calcium	188.60	237.38	166.24	144.92	113.54	56.961	61.860	75.623	0.2607
Strontium	309.67	212.01	180.66	140.38	113.49	77.87	150.06	136.93	insol.
Barium	198.33	217.06	124.62	75.654	58.168	56.226	124.67	112.95	insol.

TABLE 3.10. HYDRATES AND AMMONIATES OF THE ALKALINE EARTH PERCHLORATES

Compound	ΔH Formation* (kcal/mole adduct)	Compound	ΔH Formation
Mg(ClO ₄) ₂ ·2H ₂ O	13.509 ^a	Sr(ClO ₄) ₂ ·4H ₂ O	13.2 ^b
Mg(ClO ₄) ₂ ·4H ₂ O	24.724 ^a	Ba(ClO ₄) ₂ ·3H ₂ O	8.63 ^b
Mg(ClO ₄) ₂ ·6H ₂ O	32.708 ^a	Mg(ClO ₄) ₂ ·6NH ₃	99.1 ^c
Mg(ClO ₄) ₂ ·6H ₂ O	38.37 ^b	Ca(ClO ₄) ₂ ·6NH ₃	72.6 ^c
Ca(ClO ₄) ₂ ·4H ₂ O	15.485 ^b	Sr(ClO ₄) ₂ ·6NH ₃	64.9 ^c
Sr(ClO ₄) ₂ ·2H ₂ O	9.5 ^b	Ba(ClO ₄) ₂ ·6NH ₃	54.3 ^c

* ΔH formation from anhydrous salt and water or ammonia.^a Smith, G. F., Rees, O. W. and Hardy, V. R.⁸⁶^b Smeets, C.⁷⁸^c Smeets, C.⁸¹

temperature-weight curve. The product in this case is magnesium oxide. Another study⁹⁵ of the thermal decomposition of magnesium, calcium and barium perchlorates indicated that in the first case the final product is (MgCl)₂O. The calcium salt gives calcium chloride with traces of calcium oxide and barium perchlorate decomposes to barium chloride only.

The solubilities of a number of alkaline earth perchlorates in various solvents have been measured by Willard and Smith⁹² and are shown in Table 3.9.

All of the alkaline earth perchlorates, with the possible exception of beryllium perchlorate, for which no data are available, form both hydrates and ammines. Heats of formation for a number of these have been measured and are given in Table 3.10. In addition to those tabulated the following ammines have been reported⁸¹:

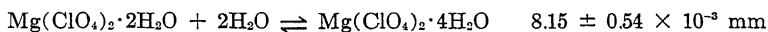
Mg(ClO ₄) ₂ ·2NH ₃	Sr(ClO ₄) ₂ ·10NH ₃
Ca(ClO ₄) ₂ ·2NH ₃	Sr(ClO ₄) ₂ ·12NH ₃
Ca(ClO ₄) ₂ ·3NH ₃	Ba(ClO ₄) ₂ ·2NH ₃
Sr(ClO ₄) ₂ ·NH ₃	Ba(ClO ₄) ₂ ·5NH ₃
Sr(ClO ₄) ₂ ·2NH ₃	Ba(ClO ₄) ₂ ·9NH ₃
Sr(ClO ₄) ₂ ·7NH ₃	

The decammine and dodecammine of strontium perchlorate are unstable at room temperature. A reported heptammine of magnesium perchlorate is

probably the result of a typographical error and the existence of a tetramine of calcium perchlorate has been disputed.^{81, 85}

The heat of hydration of magnesium perchlorate in going from the anhydrous state to the hexahydrate is greater than the heat evolved by phosphorus pentoxide in going to orthophosphoric acid. This salt would thus be expected to be as efficient as phosphorus pentoxide as a drying agent, a fact which has been verified.⁸⁶ The great affinity of this salt for water is probably the cause of some dispute over its solubility in ethyl ether. Willard and Smith⁹² reported a solubility of 0.29 g/100 g ether (Table 3.9). Later, Rowley and Seiler⁶⁸ reported a solubility of 0.06 per cent for this system, attributing the previous high value to the presence of moisture. A third value⁵ of 20 to 25 per cent was published in 1948. Extreme care must be exercised to insure that both solvent and solute are anhydrous in working with magnesium perchlorate.

A trihydrate of magnesium perchlorate was reported by Willard and Smith⁹¹ and disputed by Moles and Roquero,⁵⁴ who concluded that the supposed trihydrate was actually mixed crystals. Copeland and Bragg,¹⁵ in an intensive investigation of the hydrates of this salt, found no evidence for the existence of a trihydrate. These workers measured aqueous vapor pressures for the equilibria



at 23°C. The vapor pressure of the saturated solution was found to be 81×10^{-3} mm and an upper limit of 0.56×10^{-3} mm was set for the equilibrium between the dihydrate and the anhydrous salt.

Mono-, di- and trietherates of magnesium perchlorate have been reported.⁶⁸ The salt is reported to have a high heat of solution and the monoetherate is stable above 100°C.

The solubility of magnesium, strontium and calcium perchlorates in water has been measured for the temperature range 0 to 50°C.⁴³ A linear relationship was found between temperature and solubility and between $\log \mu$ (where μ is the molar quantity) and $1/T$. Partial molar enthalpies and entropies were calculated from the slopes of the latter curves. Determination of pH values of aqueous solutions² of the alkali metal perchlorates showed that pH was a complex function of molality.

Magnetic susceptibilities of the alkaline earth perchlorates have been measured by Pacault and Stoltz⁵⁶ and are given in Table 3.11. Magnesium, calcium, strontium and barium perchlorates form hexapyridine complexes.⁷⁷ All of these except the magnesium compound are deliquescent, and it is highly hygroscopic.

Hydroxyperchlorates of magnesium, calcium and barium have been re-

TABLE 3.11. MAGNETIC SUSCEPTIBILITIES OF GROUP II PERCHLORATES ($\times 10^6$)⁵⁶

Salt	Molar	Cationic	Anionic
Mg(ClO ₄) ₂	65.0	10.1	27.5
Ca(ClO ₄) ₂	70.5	16.0	27.2
Sr(ClO ₄) ₂	81.4	24.5	28.5
Ba(ClO ₄) ₂	94.7	38.2	28.3

ported by Hayek and Schnell.²⁹ These were formed by dissolving the metal oxides in the corresponding perchlorates. The pH, oxide content and absorption spectra of the resulting complex solutions were studied. The solid phases were identified as basic salts by x-ray analysis.

Aqueous solutions of all of the Group II perchlorates have been used as solvents for cellulose.^{20, 22}

The preparation and properties of magnesium perchlorate and its use as a drying agent are reported in detail by Willard and Smith.⁹¹ The Raman spectrum of monocrystals of magnesium perchlorate has been determined.^{45, 90}

Bacarella and co-workers² studied the absorption of organic vapors by anhydrous magnesium perchlorate at 25°C. They found that methanol, ethanol, acetone, pyridine, acetonitrile, ammonia and nitromethane are all quantitatively absorbed by the salt. The absorption of 1,4-dioxane and chloroform was not quantitative. On this basis it is assumed that magnesium perchlorate could be a general reagent for polar vapors.

Tables of revised values for osmotic and activity coefficients of magnesium perchlorate were published by Stokes in 1948.⁸⁷

Conductances of solutions of magnesium perchlorate have been measured in normal propyl and isopropyl alcohols,⁷⁰ methanol-acetone,⁷⁴ water,⁷¹ and in acetone, methyl alcohol and nitromethane.⁶⁹ The conductances of acetone solutions of calcium perchlorate have also been measured.⁶⁹

The basic calcium salts $3\text{Ca}(\text{OH})_2 \cdot \text{Ca}(\text{ClO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2 \cdot \text{Ca}(\text{ClO}_4)_2 \cdot 2\text{-}4\text{H}_2\text{O}$ have been reported⁴⁰ and their crystal structures have been determined.⁵⁹

Coefficients of adiabatic compressibility of aqueous solutions of calcium and strontium perchlorates have been reported.²⁵ Conductances of solutions of strontium perchlorate in methanol-acetone have been measured.⁷⁴

The preparation of barium perchlorate trihydrate and its use as a desiccant have been described by Smith.⁸³ Refractometric measurements of crystals of the trihydrate⁹⁴ show the refractive indices to be 1.533 and 1.532 and the molar refraction 41.60.

Preparation of the anhydrous salt and its use as a drying agent and ammonia absorbent have been described.⁸² The barium amino perchlorates

TABLE 3.12. DISSOCIATION PRESSURES OF BARIUM AMMINO PERCHLORATES⁸⁰

Equilibrium System	Pressure of Ammonia (mm)						
	-79°C	-21.5°C	0°C	20°C	40°C	60°C	80°C
Ba(ClO ₄) ₂ -Ba(ClO ₄) ₂ ·2NH ₃			4	8	20	54	106
Ba(ClO ₄) ₂ ·2NH ₃ -Ba(ClO ₄) ₂ ·5NH ₃		4	16	60	182		
Ba(ClO ₄) ₂ ·5NH ₃ -Ba(ClO ₄) ₂ ·6NH ₃		28	64	125	190		
Ba(ClO ₄) ₂ ·2NH ₃ -Ba(ClO ₄) ₂ ·6NH ₃						434	780
Ba(ClO ₄) ₂ ·6NH ₃ -Ba(ClO ₄) ₂ ·9NH ₃	2	120	390				

have been studied extensively by Smeets,⁸⁰ who measured the equilibrium dissociation pressures at several temperatures, as shown in Table 3.12.

The electrolysis of barium perchlorate has been studied in several organic solvents and its conductance measured in furfural, "Cellosolve" and ethylene glycol.¹²

Anhydrous barium perchlorate shows two crystal transitions, $\alpha \rightarrow \beta$ at 284°C and $\beta \rightarrow \gamma$ at 360°. It forms a eutectic melting at 310°C with sodium perchlorate.⁹⁶ The eutectic occurs at 43 mole per cent barium perchlorate. The basic salt Ba(OH)ClO₄ has been reported.⁶⁴

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4. METAL PERCHLORATES

A large number of metal perchlorates other than those discussed in Chapter 3 have been prepared and studied for a variety of uses. Very few thermodynamic data have been reported on these compounds, however.

Perchlorates are, in general, quite soluble in water and in many organic solvents. Approximate solubilities of a number of perchlorates in furfural and "Cellosolve" (monoethyl ether of ethylene glycol) have been determined by Chaney and Mann¹⁵ and are shown in Table 4.1. These same workers measured the conductances of some of these salts in both furfural and cellosolve, as well as a few in pyridine and in glycol. They measured several electrode potentials in furfural and Cellosolve (based on a value of -0.122V for the Pb-Pb^{++} electrode) and electrodeposited several metals from solutions of their perchlorates in these solvents.

The pyridine complexes of a number of metal perchlorates were prepared by Sinha and Ray⁹¹ and are described as shown in Table 4.2.

West¹⁰⁹ determined the crystal structures of the hexahydrates of a number of bivalent metal perchlorates. Those listed in Table 4.3 have hexagonal structures that can be derived from lithium perchlorate trihydrate by removing half of the lithium atoms and replacing the remainder with the metal. The crystals are twinned so that the water-perchlorate lattice is continuous by virtue of its high symmetry, while the metal lattice, with lower symmetry, is discontinuous at the twinning boundary. Mercuric perchlorate hexahydrate is trigonal with refractive indices 1.511 and 1.509 while copper perchlorate hexahydrate is monoclinic with $\alpha = 1.495$, $\beta = 1.505$ and $\gamma = 1.522$.

Hydroxyperchlorates of magnesium, calcium, barium, cadmium, zinc and bivalent lead, mercury and copper were made by Hayek and Schnell⁴⁰ by dissolving the oxides in the corresponding perchlorates. Absorption spectra of the resulting complex solutions were studied and the solid phases were identified as basic salts by x-ray analysis.

A number of specific compounds are described briefly below.

Aluminum Perchlorate. The salt forms hydrates with 15, 9, 6 and 3 moles of water. The lower hydrates are all extremely hygroscopic and the anhydrous salt is prepared by dehydration of the hydrates with considerable difficulty. The densities of the various hydrates have been reported by Moles and Barcia⁶⁸ as 1.764, 1.924, 2.020 and 2.145 for the 15, 9, 6 and 3 hydrates, respectively. The anhydrous salt has a density of 2.209. These same authors report melting points of 76.2, 85.3 and 120.8°C for the 15, 9 and 6 hydrates, respectively. The trihydrate is not a true hydrate. It decomposes on fusion and the water belongs to the anion.

TABLE 4.1. SOLUBILITY OF METALLIC PERCHLORATES
IN VARIOUS SOLVENTS¹⁵

Grams of solute per 100 cc of solvent

Salt	Furfural	"Cellosolve"	Water
Ba(ClO ₄) ₂	50	100+	—
Cd(ClO ₄) ₂ ·6H ₂ O	80	145	478
Cu(ClO ₄) ₂ ·6H ₂ O	70	100+	—
Cu(ClO ₄) ₂ ·2H ₂ O	20+	—	259
Co(ClO ₄) ₂ ·6H ₂ O	60	110	292
Mn(ClO ₄) ₂ ·6H ₂ O	90	130	268
Ni(ClO ₄) ₂ ·6H ₂ O	60	100+	267
Ni(ClO ₄) ₂ ·2H ₂ O	20	35	—
AgClO ₄	40	125	540
Pb(ClO ₄) ₂	25	105	—
Zn(ClO ₄) ₂ ·6H ₂ O	85	130	—

TABLE 4.2. PYRIDINE COMPLEXES OF METAL PERCHLORATES⁹¹

Compounds	Properties
AgClO ₄ ·4C ₅ H ₅ N	Colorless cubic crystals. Fairly stable.
Cu(ClO ₄) ₂ ·4C ₅ H ₅ N	Small violet-blue crystals. Stable. Not hygroscopic.
Mg(ClO ₄) ₂ ·6C ₅ H ₅ N	Colorless crystals. Extremely hygroscopic.
Ca(ClO ₄) ₂ ·6C ₅ H ₅ N	Colorless crystals. Highly deliquescent in moist air. Unstable.
Sr(ClO ₄) ₂ ·6C ₅ H ₅ N	Colorless crystals. Highly deliquescent in moist air. Unstable.
Ba(ClO ₄) ₂ ·6C ₅ H ₅ N	Colorless crystals. Deliquescent, but less so and more stable than Ca and Sr compounds.
Zn(ClO ₄) ₂ ·4C ₅ H ₅ N	Colorless hexagonal pyramids. Fairly stable. Not hygroscopic.
Cd(ClO ₄) ₂ ·6C ₅ H ₅ N	Stable colorless crystals. Not deliquescent.
Hg(ClO ₄) ₂ ·6C ₅ H ₅ N	Colorless crystals. Not hygroscopic. Quite stable.
Mn(ClO ₄) ₂ ·8C ₅ H ₅ N	Lilac crystals. Not deliquescent. Partially hydrolyzed with water.
Ni(ClO ₄) ₂ ·6C ₅ H ₅ N	Pale green crystals. Stable. Not very hygroscopic.
Co(ClO ₄) ₂ ·6C ₅ H ₅ N	Pink hexagonal prisms. Soluble in chloroform. Fairly stable.

The anhydrous salt can be prepared from the trihydrate by drying at 145 to 155°C over phosphorus pentoxide *in vacuo*.³⁵ It has also been made by distilling anhydrous perchloric acid onto anhydrous aluminum chloride and removing the excess perchloric acid in a stream of nitrogen.³⁷ The compound prepared in this way is contaminated with a small amount of aluminum chloride and could not easily be further purified by recrystallization from organic solvents in which it is very soluble. A nearly theoretical yield of anhydrous aluminum perchlorate can be obtained by the reaction of an-

TABLE 4.3. CRYSTAL STRUCTURES OF SOME TRANSITION METAL PERCHLORATES¹⁰⁹

Metal M in $M(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	Refractive Indices		Cell Dimensions (Å) (Hexagonal System)	
	n_o	n_e	a	c
Mn	1.492	1.475	15.70	5.30
Fe	1.493	1.478	15.58	5.24
Co	1.510	1.490	15.52	5.20
Ni	1.518	1.498	15.46	5.17
Zn	1.508	1.487	15.52	5.20
Cd	1.489	1.480	15.92	5.30

hydrous aluminum chloride with silver perchlorate in an organic solvent such as methanol or benzene.¹

The thermal decomposition of the hexahydrate was reported by Zinov'ev and Cludinova.¹¹⁵ These workers reported a melting point of 82°C for the salt. Dehydration occurs simultaneously with hydrolysis at 178° to yield the basic salt $\text{Al}(\text{OH})(\text{ClO}_4)_2$. At 262 and 264°C two final stages of decomposition occur in rapid succession yielding Al_2O_3 as the final product. Marvin and Woolaver⁶⁶ also found Al_2O_3 to be the final product of decomposition. Conductivity measurements in aqueous solution show the salt to be completely ionized in dilute solutions.³⁹ Conductivities have been determined in nitrobenzene, acetonitrile and Cellosolve. Electrolysis of these solutions failed to yield a deposit of aluminum.^{6, 37} The Raman spectra of aqueous solutions have been reported.⁶⁵

Antimony Perchlorate. This salt was prepared by Fichter and Jenny²⁷ as a trihydrate by the reaction of freshly precipitated $\text{Sb}(\text{OH})_3$ with perchloric acid. The compound decrepitates strongly when heated above 60°C with the formation of higher oxides of antimony.

Bismuth Perchlorate. An interesting reaction takes place between perchloric acid and bismuth.⁷³ If bismuth is dipped in perchloric acid and then heated above a flame, a brownish coating appears on the surface which, upon further heating, explodes violently, leaving a clean surface. If bismuth is activated by heating in perchloric acid, then cooled and allowed to remain in the acid, it always explodes sooner or later. Exposure to air for some time or dipping in water causes the brownish layer to disappear and the explosive property is lost. The explosion is definitely identified as a surface phenomenon but its nature is unknown.

The pentahydrate of bismuth perchlorate can be prepared by slowly dissolving bismuth oxide in 40 per cent perchloric acid.²⁷ Solution of this salt in water and evaporation over calcium chloride gave $\text{BiOClO}_4 \cdot 3\text{H}_2\text{O}$ which passes readily into $\text{BiOClO}_4 \cdot \text{H}_2\text{O}$ on further drying. The last of the water can be removed by drying at 80 to 100°C.

Smith⁹⁶ has measured the conductivity of solutions of bismuth perchlorate and its various basic salts and has reported the emf of various bismuth half-cells.

Holmqvist⁴⁹ studied the dissociation of bismuth perchlorate solutions with the quinhydrone electrode. He assumed that the complex compounds $\text{Bi}_2(\text{OH})_4(\text{ClO}_4)_2$ and $\text{Bi}_2(\text{OH})_5\text{ClO}_4$ exist in solution, and isolated a compound of the formula $\text{Bi}_2(\text{OH})_3\text{OClO}_4$.

The Raman spectrum of bismuth perchlorate solution in water has been reported.⁶⁵

Cadmium Perchlorate. The potentials of cadmium perchlorate cells were measured by Jena and Prasad.⁵³ They found that the salt is completely dissociated in aqueous solution up to a concentration of 0.1 *M*. The salt forms a six-ammoniate.²⁵ The Raman spectrum of the crystalline salt indicates that it has trigonal symmetry.¹⁰⁵ The pH of aqueous solutions is a complex function of molality.⁵⁶

Cobalt Perchlorate. Cobaltic perchlorate has been prepared from cobaltous perchlorate both electrolytically and by fluorination at 0°C.²⁶ Extraction of cobaltous perchlorate from aqueous solutions by 2-octanol was studied by Moore and co-workers.⁶⁹

Chromium Perchlorate. This salt forms hydrates with 10, 9, 6, 5 and 3 moles of water.⁹ They were prepared by reacting chromium hydroxide with perchloric acid.

Copper Perchlorate. The heat of formation of copper perchlorate in aqueous solution is -19.0 kcal/mole.⁸⁵ The salt forms hydrates with 7, 6, 4 and 2 moles of water.⁷⁷ The density of the hexahydrate at 23°C is 2.225 and its solubility is 54.3 per cent. The molar heat of solution is -4.6 kcal/mole. The system copper perchlorate-perchloric acid-water has been studied by Smeets⁹⁵ for possible complex acid salts. However, no such complexes were found. The melting point of the hexahydrate was reported by this worker to be 82.3°C. Evaporation above that temperature gives the tetrahydrate. The basic salt $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{CuO} \cdot \text{H}_2\text{O}$ was prepared by Beeke and Goldwasser⁷ by electrometric titration of copper perchlorate solutions with sodium hydroxide. The solubility product of cupric hexahydroxy perchlorate has been determined.⁷¹ The magnetic properties of aqueous solutions of cupric perchlorate have been studied.⁸ Portillo⁷⁶ prepared the complex compounds $\text{Cu}(\text{ClO}_4)_2 \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{ClO}_4)_2 \cdot 4\text{NH}_3$, $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{NH}_3$, $\text{Cu}(\text{ClO}_4)_2 \cdot 5\text{NH}_3 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{ClO}_4)_2 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$, $\text{Cu}(\text{ClO}_4)_2 \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}$ and $3\text{Cu}(\text{ClO}_4)_2 \cdot 10\text{NH}_3$ and reported the density, solubility, cryoscopic dissociation and heat of solution for each.

Ephraim and Bolle²⁴ measured the ammonia pressure over copper perchlorate hexammoniate as a function of temperature and determined the heat of dissociation to be 9.8 kcal/mole. The heats of dissociation of the

pyridine complexes $\text{Cu}(\text{ClO}_4)_2 \cdot 6$ and $\cdot 4\text{C}_5\text{H}_5\text{N}$ were measured by Sinha and Ray.⁹³ From plots of $\log p$ against $1/T$ these values were found to be 8,450 and 11,640 cal/mole, respectively. The composition and stability of these complexes in aqueous solution were reported by the same authors.⁹²

Gallium Perchlorate. Foster²⁹ prepared the compounds $\text{Ga}(\text{ClO}_4)_3 \cdot 9.5$ and $\cdot 6\text{H}_2\text{O}$ by dissolving gallium in hot concentrated perchloric acid. The properties of the compounds are described. Gallium perchlorate forms a complex with urea⁶² of the composition $\text{Ga}[\text{CO}(\text{NH}_2)_2](\text{ClO}_4)_3$, melting point 179°C , in nonaqueous solvents. In water urea precipitates $\text{Ga}(\text{OH})_3$. A basic compound of the probable composition $3\text{Ga}_2\text{O}_3 \cdot \text{Ga}(\text{ClO}_4)_3$ was obtained by dehydration of gallium perchlorate hydrates. The activity coefficient of gallium perchlorate in aqueous solutions has been measured⁷⁵ and isopiestic studies have been made.⁷⁴

Iron Perchlorates. Ferrous perchlorate hexahydrate was prepared by Lindstrand⁵⁸ by the reaction of 70 per cent perchloric acid on ferrous sulfide in an atmosphere of carbon dioxide or nitrogen. A 45 per cent yield of the hexahydrate was obtained in the form of long green crystals. The solubility of this compound in water is 978 g/l. at 0°C and 1161 g at 60° . The solubility in ethanol at 20°C is 865.4 g/l. The compound can be oxidized with air in aqueous solution.

Ferric perchlorate decahydrate was prepared from ferric hydroxide in an excess of 70 per cent perchloric acid. Its solubility in water is 1198 g/l. at 0°C and 1570 g/l. at 60° . The hydrolysis constant for the reaction $\text{Fe}^{++} + \text{H}_2\text{O} \rightleftharpoons \text{FeOH}^+ + \text{H}^+$ was determined, also by Lindstrand.⁶⁰

Ferrous perchlorate has been used as a reductant in glacial acetic acid for the determination of chromium trioxide and sodium permanganate.⁴⁸ The thermal decomposition of ferric perchlorate was studied gravimetrically by Marvin and Woolaver,⁶⁶ who found the final product to be ferric oxide.

The hydrolysis of ferric perchlorate was studied by Lindstrand,⁵⁹ who measured the hydrolysis constant and determined the heat of the reaction $\text{Fe}^{+++} + \text{H}_2\text{O} \rightleftharpoons \text{FeOH}^{++} + \text{H}^+$ to be 18.2 kcal.

Sutton¹⁰¹ found spectrophotometric evidence for the formation of a complex between ferric ion and perchlorate ion in solutions of ionic strength greater than unity.

The solution of iron in perchloric acid and the species formed in the reaction were reported by Canić and co-workers.^{13, 55}

Some organic complexes of iron perchlorate were reported by Weinland and Loebich.¹⁰⁷

Lead Perchlorate. The preparation and properties of lead perchlorate and the basic salt $\text{Pb}_3(\text{OH})_4(\text{ClO}_4)_2$ were reported by Willard and Kassner.¹¹¹ The salt forms hydrates with 1 and 2 moles of water. The anhydrous

salt was prepared from the trihydrate by several stages of drying over phosphorus pentoxide. An anhydrous solution of the salt in methyl alcohol was explosive.

The solubility of lead perchlorate in water at 27°C is 81.472 g/100 g of solution and the density of the saturated solution is 2.7753. Aqueous solutions of lead perchlorate were proposed by Thiel and Stoll¹⁰² as a substitute for Thoulet's solution for density determinations.

A number of basic lead perchlorates have been reported and studied.^{32, 80, 106, 108} The first known complex perchlorate anions were formed from lead perchlorate.¹⁰⁶

Manganese Perchlorate. This salt forms pale pink deliquescent needle prisms of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$.¹⁹ The crystals melt at 155°C and begin to decompose at 165° with the evolution of water vapor, oxygen and oxides of chlorine. The decomposition is rapid at 230°C with the final product being manganese dioxide. The anhydrous salt could not be isolated in the pure state.

Mercurous Perchlorate. This salt forms two hydrates,⁷² one with four and one with two waters of crystallization. The transition point between the two is 36°C. Hydrolysis occurs in three stages resulting in mercurous oxide as the final product. In highly concentrated solutions abnormal dissociation is indicated both by conductance and by potentiometric methods. The pH of aqueous solutions has been reported.⁵⁶

Nickel Perchlorate. A hexammine of nickel perchlorate was studied by Ephraim²² and the heat of dissociation determined. The visible spectrum of the salt was determined by Veeraiah and Qureshi¹⁰³ in aqueous solution. The extraction of nickel perchlorate from aqueous solutions by 2-octanol has been studied.⁶⁹

Palladium Perchlorate. This salt, previously known only in aqueous perchloric acid solution, was first isolated as a deliquescent crystalline tetrahydrate by Livingstone.⁶¹ It was prepared by dissolving palladium sponge in concentrated nitric acid followed by heating to fumes with 72 per cent perchloric acid. The absorption spectrum and conductance in 1 *M* perchloric acid were determined.

Rare Earth Perchlorates. Spectra from 260 to 1200 $\text{m}\mu$ of aqueous solutions of the perchlorates of praseodymium, neodymium, samarium, europium, gadolinium, dysprosium, erbium and ytterbium have been reported.⁵⁷ Transference numbers, equivalent conductances, activity coefficients and densities of aqueous solutions of eight rare earth perchlorates were reported by Spedding and Jaffe.⁹⁸

Wilke-Dörfurt and Schliephake¹¹⁰ prepared the hexaantipyrine perchlorates of lanthanum, neodymium, cerium, praseodymium and yttrium. These workers also prepared rose-colored neodymium perchlorate hexahy-

hydrate. This compound loses most of its water at 170°C and becomes exceedingly hygroscopic.

An attempt to prepare solid ceric perchlorate by concentration of its aqueous solution was unsuccessful.²⁸ A basic compound with the probable formula $\text{Ce}_2\text{O}_3(\text{ClO}_4)_2 \cdot 12\text{H}_2\text{O}$ was crystallized from a very concentrated solution at 100°C. A study of the near ultraviolet absorption spectra⁴¹ of aqueous solutions of cerous perchlorate revealed evidence for the existence of a CeClO_4^{+2} complex. The values of the thermodynamic constants for the reaction $\text{Ce}^{+3} + \text{ClO}_4^- \rightleftharpoons \text{CeClO}_4^{+2}$ were calculated. Studies of the photochemical reduction of ceric- to cerous perchlorate¹⁸ and of the photochemical oxidation of cerous- to ceric perchlorate⁴² have been reported. The oxidation of ethanol³ and 2,3-butanediol²⁰ by ceric perchlorate has been studied.

Gadolinium perchlorate octahydrate, a very deliquescent compound, was reported and described by Sarkar.^{88, 89}

The Raman spectrum,⁶⁵ apparent molar refraction, dispersion, volume and the partial molal volume of lanthanum perchlorate in aqueous solution have been determined.⁸¹

Rhodium Perchlorate. Rhodium perchlorate hexahydrate was reported by Ayres and Forrester.⁵ It is light yellow, acicular and hygroscopic. X-ray powder data indicate face-centered cubic structure.

Selenium Perchlorate. The basic compound $\text{Se}(\text{OH})_3\text{ClO}_4$ was prepared by Arlman⁴ by dissolving selenious acid in perchloric acid. The compound melts at 33°C and is very hygroscopic. The heat of solution is given as 4.8 kcal and the heat of formation from the simple acids is 11.4 kcal. The heat of formation from the elements is -149.0 kcal.⁸⁴

Silver Perchlorate. Silver perchlorate can be prepared by heating silver nitrate with a large excess of 72 per cent perchloric acid, driving off the nitric acid and recrystallizing from water or by reacting silver oxide with perchloric acid, concentrating the solution and crystallizing the salt. Silver perchlorate is very deliquescent and forms a monohydrate which can be dehydrated at 43°C.

The anhydrous salt is very light-sensitive but the presence of small amounts of perchloric acid gives a strong stabilizing effect toward light. The solubility is 557 g of silver perchlorate in 100 g of water at 25°C. The solubility and the density and refractive indices of saturated solutions were determined from 0 to 35°C by Smith and Ring.⁹⁷

The heat of formation of the salt is -7.75 kcal/mole.⁸⁶ It is thus considerably less stable than silver chloride which has a heat of formation of -30.4 kcal/mole. This instability has resulted in explosions from grinding or breaking up cakes of the salt. Brinkley¹¹ reported a violent explosion which occurred while breaking up a cake of silver perchlorate which had

TABLE 4.4. SOLUBILITY OF SILVER PERCHLORATE IN ORGANIC SOLVENTS AT 25°C

Solvent	Solubility (g/100 g solvent)	Ref.
Benzene	5.28	45
Toluene	101	47
Aniline	5.28	46
Pyridine	26.4	64

been recrystallized from benzene. In this case the detonation involved the benzene addition compound. Hein⁴³ experienced an explosion from a filter cake of silver perchlorate which was being pulverized in a mortar. Analytical examination of the perchloric acid from which the salt was prepared showed no chloride, chlorate or organic compounds. The silver nitrate used contained only spectroscopic traces of copper and iron. The presence of etherate in the cake was ruled out. It was concluded therefore that the explosion was due to silver perchlorate only.

This salt has received considerable attention because of its unique solubility in organic solvents including aromatic hydrocarbons. The salt is soluble in toluene, benzene, nitrobenzene, chlorobenzene, glycerin, and glacial acetic acid. It is insoluble in chloroform, carbon tetrachloride, and ligroin.⁴⁴ The solubility in a number of organic solvents is given in Table 4.4.

Silver perchlorate has been used to prepare mixtures of anhydrous perchloric acid with various organic compounds. Dry hydrogen chloride is bubbled through a solution of silver perchlorate in the organic solvent. Silver chloride precipitates, leaving a mixture of perchloric acid and solvent. The densities of 5, 10, and 15 per cent aqueous solutions were measured by Mazzucchelli and Rossi⁶⁷ at 15 and 25°C. The density of the solutions at 15° is given by the equation

$$d_{15} = 0.99913 + 7.9183 \times 10^{-3}p + 8.762 \times 10^{-6}p^2 - 5.35 \times 10^{-7}p^3$$

where p = gram-% of anhydrous salt. The heats of dilution of aqueous silver perchlorate solutions have been measured.⁵¹

Hill and co-workers⁴⁵⁻⁴⁷ studied the systems silver perchlorate-water-benzene, silver perchlorate-water-toluene and silver perchlorate-water-aniline. Macy⁶⁴ has studied the system silver perchlorate-water-pyridine. Ternary phase diagrams are given for all of these systems. Silver perchlorate forms the following complexes: $\text{AgClO}_4 \cdot \text{C}_6\text{H}_6$; $\text{AgClO}_4 \cdot \text{C}_7\text{H}_8$; $\text{AgClO}_4 \cdot 1,2,3$ and $6\text{C}_6\text{H}_5\text{NH}_2$; $\text{AgClO}_4 \cdot 2\text{Py}$; $4\text{AgClO}_4 \cdot 9\text{Py}$; $\text{AgClO}_4 \cdot 4\text{Py}$; and $\text{AgClO}_4 \cdot 3\text{dioxane}$. The crystal structure of this last compound was determined by Prosen and Trueblood.⁷⁸

Robertson⁸² found that in a solution of silver perchlorate in water-satu-

TABLE 4.5. CONDUCTANCES OF SILVER PERCHLORATE
IN ORGANIC SOLVENTS

Solvent	Λ_0	Ref.	Solvent	Λ_0	Ref.
Acetone	181.55	36	Nitromethane	116	114
Acetone + 1% pyridine	167.42	36	Methanol	121.15	16
Acetone + 1% picoline	166.33	36	Ethanol	51.45	17
Acetone + 1% collidine	161.16	36	Nitrobenzene	38.4	70
Pyridine	81.9	36	Furfural	50	15
Benzene	150	36, 63	"Cellosolve"	approx. 35	15

rated benzene the molecular species is approximately $(\text{AgClO}_4 \cdot \text{H}_2\text{O})_3$. The partition law does not hold in this system. The conductances of solutions of silver perchlorate in a number of organic solvents have been measured and are given in Table 4.5.

The salt is appreciably associated in most of these solutions, but is a strong electrolyte in liquid hydrogen fluoride,³⁰ as well as in liquid hydrogen cyanide⁵² in which several of its reactions have been studied. The electrode potential of the silver electrode has been measured in furfural and Cellosolve.¹⁵ The dielectric constants, densities, and molar polarizations of dilute solutions of silver perchlorate in benzene have been reported.^{33, 50, 112, 113} In very dilute solutions the dielectric constant approaches the theoretical value for the ion pair.

Anders² determined freezing point curves for benzene-acetic acid mixtures and the solubility and freezing point depressions of silver perchlorate in the mixed solvents, in which the salt was found to be associated. The compositions of all phases were determined. The spectra of solutions of silver perchlorate in acetone have been reported⁷⁹ and are discussed under lithium perchlorate.

Gomberg³⁴ reported the reaction between silver perchlorate and iodine in benzene solution to give chlorine tetroxide. Later workers,¹⁰ however, felt that the reaction forms iodine perchlorate which subsequently reacts with benzene to give iodobenzene and perchloric acid. Solutions of silver perchlorate will absorb much more acetylene than solutions of silver nitrate of similar concentration before a permanent precipitate appears.¹⁰⁴ Silver perchlorate reacts slowly with methyl iodide to give methyl perchlorate and with benzyl bromide to give benzyl perchlorate.¹² The salt acts in three different ways¹⁴ in organic reactions: (1) by replacing Cl by ClO_4 , (2) by forming complexes with nucleophilic substances and catalyzing reactions of the Friedel-Crafts type, and (3) by oxidation in which Ag^+ and not ClO_4^- is the oxidant.

Thallium Perchlorate. This compound exhibits a crystal transition at 266°C and melts at 501°C.⁸⁷ Its conductivity has been measured in nitromethane.¹¹⁴ Osmotic and activity coefficients have been tabulated.⁸³

Tin Perchlorate. Perchlorate ion is reduced by stannous chloride. The mechanism of the tungstate-catalyzed reaction has been studied by Haight.³⁸

Titanium Perchlorate. No titanium perchlorate has been isolated. Titanium (III) reduces perchlorate ion in dilute solution. The kinetics of the reaction, which proceeds stepwise through various basic salts, has been studied by Duke and Quinney.²¹

Vanadium Perchlorate. No vanadium perchlorates have been isolated. Solutions of vanadium (III) and vanadium (IV) perchlorate were prepared by Furman and Garner³¹ and the absorption spectra studied. The kinetics of the oxidation of vanadium (II) and vanadium (III) ions by perchlorate ion has been studied by King and Garner.⁵⁴

Zinc Perchlorate. The dissociation pressure at various temperatures of zinc perchlorate ammine was measured by Ephraim and Bolle²³ and the heat of formation calculated. The composition of the ammoniate as a function of temperature has been reported by Ephraim and Zapata.²⁵

Conductances of moderately concentrated solutions of zinc perchlorate in the mixed solvent methanol-acetone have been measured.⁹⁰ Osmotic and activity coefficients were reported by Stokes.^{99, 100} The pH of aqueous solutions is a complex function of molality.⁵⁶

Sircar and Prasad⁹⁴ measured the potentials of zinc perchlorate cells at a number of concentrations of zinc perchlorate. They found the mean transport number of perchlorate anion to be 0.595. The fact that the transport number does not change appreciably with concentration up to 0.1 *M* indicates that zinc perchlorate is completely dissociated.

The Raman spectrum of zinc perchlorate crystals was reported by Weil and Mathieu.¹⁰⁵

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5. MISCELLANEOUS PERCHLORATES

INORGANIC PERCHLORATES

Hydrazine Perchlorate

This compound was first made by Salvadori⁶⁸ by neutralizing a dilute solution of hydrazine with dilute perchloric acid. The compound formed is a hydrate, $\text{N}_2\text{H}_5\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, which is stable up to 60.5°C. The anhydrous salt can be recrystallized from alcohol. It is a white crystalline solid which melts at 137 to 138°C to a colorless liquid.⁸ Decomposition begins at 145°C and is complete by 230° if heating is careful; otherwise a strong deflagration occurs. Shock or friction cause violent detonation. The anhydrous salt has a shock sensitivity comparable to that of initiating explosives. The hydrate, however, is considerably less sensitive.

The density of the salt is 1.939 and the solubility in 100 g saturated aqueous solution is 23.6 g at 0°C, 68.9 g at 40°, 87.4 g at 60° and 93.1 g at 75°. The solubility in absolute ethanol is very slight at 0°C but is 69 g/100 g solution at 60°C. The salt is insoluble in ether, carbon tetrachloride, trichloroethylene, benzene, chloroform, and carbon disulfide. The salt is completely dissociated in water but undissociated in ethanol. The heat of formation has been calculated to lie between -42 and -43 kcal/mole. The dissociation of the hydrate into water and the anhydrous salt has been studied by Christensen and Gilbert.¹⁵ They find that the pressure of water vapor above the salt is given by the equation:

$$\log P_{\text{mm}} = -3047.6/T + 10.980 \quad T \leq 60.5^\circ\text{C}$$

The heat of dissociation is 13.95 kcal/mole and the free energy of dehydration is 1,456 cal/mole.

Maissen and Schwarzenbach⁵⁸ attempted to prepare nickel hydrazine perchlorate from nickel perchlorate and hydrazine in water solution. After 5 days a blue precipitate had formed and additional water was added. When a glass stirring rod was introduced into the suspension a violent explosion resulted.

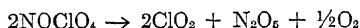
Nitrosyl Perchlorate

This compound was first prepared by Hofmann and Zedtwitz⁴⁴ by passing a mixture of nitric oxide and nitrogen dioxide into 72 per cent perchloric acid. The acid was then evaporated to 140°C (dense white fumes) and upon cooling, $\text{NOCIO}_4 \cdot \text{H}_2\text{O}$ crystallized out. The product was dried over phosphorus pentoxide in an atmosphere of nitrogen oxides, then finally

in vacuo. The compound is not very hygroscopic. The salt is orthorhombic⁵³ with the axial lengths the same as perchloric acid monohydrate:

$$\begin{aligned}a &= 9.00 \pm 0.05\text{\AA} \\b &= 5.68 \pm 0.05\text{\AA} \\c &= 7.23 \pm 0.03\text{\AA}\end{aligned}$$

The Raman spectrum¹ is that for the perchlorate ion plus a strong frequency at 2329 cm^{-1} which is assigned to the NO^+ group. The density of the compound is 2.169 g/cc .¹⁸ The heat of formation^{20, 21} is $-41.79 \pm 0.08\text{ kcal/mole}$. The salt decomposes without melting. When heated below 100°C it decomposes as shown¹⁹:



When heated at a higher temperature or if the initial reaction products remain in contact with one another for 4 or 5 days, the decomposition corresponded to the equation:



The compound reacts with water causing evolution of nitrogen oxides. With methanol, nitromethane is formed. Ethanol and acetone ignite on contact with the compound. With dry ether it reacts with gas evolution followed by explosion. Nitrosyl perchlorate reacts violently with primary amines, resulting in ignitions or explosions.⁴⁴

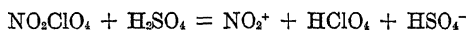
Nitryl or Nitroxyl Perchlorate

Hantzsch³⁸ reported a compound of the composition $[\text{NO}(\text{OH})_2]^+ \cdot [\text{ClO}_4]^-$ formed as a precipitate when anhydrous nitric and perchloric acids were mixed.

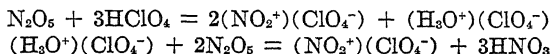
Later work by Goddard and co-workers,³¹ however, indicated that the substance obtained by Hantzsch was actually a mixture of perchloric acid monohydrate and a compound NO_2ClO_4 which had been reported by Gordon and Spinks.³⁵ Goddard separated these two compounds by fractional crystallization from nitromethane and identified the two species. The first preparation³⁵ was accomplished by mixing chlorine dioxide with a mixture of ozone and oxides of nitrogen which had resulted from the passage of dry air through an ozonizer. The compound is composed of NO_2^+ and ClO_4^- ions.¹⁷ The crystals are monoclinic with unit cell dimensions: $a = 9.25$; $b = 6.99$; $c = 7.34$.

From the Raman spectrum, Millen⁶² concluded that the compound consists entirely of NO_2^+ and ClO_4^- ions.

Gillespie²⁷ found from cryoscopic measurements in sulfuric acid that the following dissociation takes place:



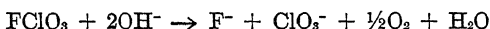
Goddard and co-workers³² prepared the pure compound from dinitrogen pentoxide and anhydrous perchloric acid by the reactions:



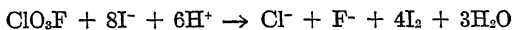
They found that the compound decomposes without exploding above 135°C, giving off NO₂. It is soluble in nitric acid from which it can be crystallized. The saturated solution in nitromethane at room temperature is about 0.08*M* and in carbon tetrachloride or chloroform 0.01*M*. The compound reacts very rapidly with water giving nitric acid and perchloric acid with a moderate evolution of heat. It reacts violently with many organic compounds causing ignitions and explosions under some conditions. It can be used in nitromethane solution to nitrate many aromatic compounds. Benzene is thus converted instantly to nitrobenzene but nitrobenzene is further nitrated only slowly. The Raman spectrum of the compound has been reported in nitric acid solution.⁴⁶

Perchloryl Fluoride

Bode and Klesper,⁷ while studying the action of fluorine on potassium chlorate at temperatures between -40 and +20°C, obtained a new compound with the empirical formula ClO₃F. They reported a melting point of approximately -110°C and a boiling point of -46°. The compound had a heat of vaporization of 4.6 kcal/mole and a Trouton's constant of 20.2. They suggested the name "chloryl oxyfluoride" and proposed the structure O₂Cl-OF. The compound was reported to react with base according to the equation:



Later Engelbrecht and Atzwanger²⁵ prepared the compound by the electrolysis of sodium perchlorate in liquid hydrogen fluoride. They determined the boiling point to be -48.1°C. They found that the compound reacted with potassium iodide solution according to the equation:



In contrast to the basic hydrolysis reaction reported by Bode and Klesper, these workers found the hydrolysis products to be perchlorate ion and fluoride ion as indicated by the equation:



This compound is surprisingly stable. It can be heated in glass to the softening point without etching the surface. The compound can be prepared by the action of fluorosulfonic acid on perchlorates in reported yields of 67 per cent.⁴ The physical properties of the compound have been ex-

TABLE 5.1. PHYSICAL PROPERTIES OF PERCHLORYL FLUORIDE

		Ref.
Melting point	$-146^{\circ}\text{C} \pm 2^{\circ}\text{C}$	26
Boiling point	-46.8°C	26, 52
Vapor pressure	$\log_{10} P_{\text{mm}} = 18.90112 - 1443.467/T -$ $4.09566 \log_{10} T$ (-120 to -40°C) $\log P$ (atm) $= 4.46862 - 1010.81/T$ (-40 to $+95.17^{\circ}\text{C}$)	52
Heat of vaporization	4.6 kcal/mole	52
Entropy of vaporization	21.97 e u	26
Liquid density	$2.266 - 1.603 \times 10^{-3} T - 4.080 \times$ $10^{-6} T^2$ g/ml T = absolute temperature	52
Critical temperature	95.13°C	26, 52
Critical pressure	53.00 atm	2, 52
Critical density	0.637 g/cm ³	26
Critical molar volume	161 cm ³	26
Dipole moment	$0.023\text{D} \pm 0.003\text{D}$	60
Heat of formation of gas at 25°C	-5.12 ± 0.68 kcal/mole	2
Entropy of gas at 25°C	66.51 e u/mole	2
Specific heat of liquid:		2
-40°C	0.229 cal/gm deg	
-10°C	0.244 cal/gm deg	
$+50^{\circ}\text{C}$	0.290 cal/gm deg	
C_p/C_v at 24°C	1.12	2
Surface tension:		70
-75.2°C	24.1 dynes/cm	
-68.5°C	22.3	
-55.6°C	21.3	
Viscosity	$\log \eta = (299/T^{\circ}\text{K}) - 1.755$ centipoises	70

tensively reported and are listed in Table 5.1. Thermodynamic functions have been calculated from 100 to 5000°K .⁶⁴ It has a dielectric strength approximately 30 per cent greater than that of sulfur hexafluoride.²

The structure of the compound has been established as FClO_3 with the oxygen and fluorine atoms all attached to the central chlorine.⁵⁵ The infrared spectrum has been reported in detail^{26, 55, 57} and assignments made for the fundamental vibration frequencies.⁵⁵ No microwave absorptions have been found.⁵⁴

Quantitative hydrolysis to fluoride and perchlorate ions can only be accomplished with concentrated base or by heating with water at 250 to 300°C in a closed tube. Its reaction with sodium or potassium metal, while vigorous, requires temperatures up to 300°C for initiation.²⁶

At elevated temperature the oxidizing power manifests itself strongly.⁵

At 150 to 300°C perchloryl fluoride reacts vigorously with a wide variety of reducing agents. It is soluble to the extent of 1 to 4 g/l. in several organic solvents. With some organic halides the solubility is much greater. Dry perchloryl fluoride is noncorrosive to many materials of construction. The wet gas, however, is corrosive to most metals.

Perchloryl fluoride reacts with aqueous or liquid anhydrous ammonia⁴⁹ to form a mixture of ammonium fluoride and ammonium perchlorylamide, $\text{NH}_4\text{NHClO}_3$. The ammonolysis in liquid ammonia is greatly accelerated by traces of sodium amide. From an alcoholic solution of ammonium fluoride plus $\text{NH}_4\text{NHClO}_3$, cesium hydroxide precipitates Cs_2NClO_3 and potassium hydroxide precipitates K_2NClO_3 . These are white crystalline solids isomorphous with the metal sulfates, have melting points above 300°C, are highly explosive and, when dry, very sensitive to flame, shock, and friction. A dilute aqueous solution of K_2NClO_3 has a pH of 12. By titration of K_2NClO_3 to pH 8.5 with dilute perchloric acid, followed by fractional crystallization, KNHClO_3 has been isolated.

A new series of organic compounds formed from ClO_3F has been reported by Inman and co-workers.^{47, 49} Perchloryl fluoride undergoes a Friedel-Crafts type of reaction with aromatic compounds to form "perchloryl" substituted compounds. In this way perchloryl benzene, $\text{C}_6\text{H}_5\text{ClO}_3$, is formed by the reaction of perchloryl fluoride with benzene in the presence of the aluminum chloride or aluminum bromide. In these reactions the aluminum halide is used up and loses its catalytic power. The over-all reaction with benzene can be written as:



The compound 2,5-dimethylperchlorylbenzene has been made by the perchlorylation of *p*-xylene. Similarly, 4-fluoroperchlorylbenzene has been made from fluorobenzene. These compounds will be discussed in more detail in the section "Organic Perchlorates."

The reaction of perchloryl fluoride with the alkali metal salts of certain active hydrogen compounds has been found to result in a new fluorination reaction in which the acid hydrogen atoms of the starting compounds were replaced with fluorine. For example, when perchloryl fluoride was passed into an alcoholic solution of the sodium salt of diethylmalinate, diethyldifluoromalinate was produced. Ethyl acetoacetate has been fluorinated to ethyl-2,2-difluoroacetoacetate in this manner and 3,3-difluoro-2,4-pentanedione and diethyl-2-fluoro-2-phenylmalinate have also been prepared.^{48, 50}

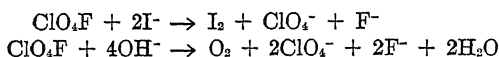
Fluoronium Perchlorate

Hantzsch³⁷ reported the compound fluoronium perchlorate $(\text{FH}_2)^+ \cdot (\text{ClO}_4)^-$ formed by reaction of anhydrous perchloric and hydrofluoric

acids. Brauer and Distler,⁸ however, were unable to repeat the preparation of this compound despite variations in the ratio of the reactants and the temperature of the reaction mixture.

Fluorine Perchlorate

Fluorine perchlorate, FClO_4 , was prepared by Rohrback and Cady⁶⁷ by the reaction of elemental fluorine with 60 per cent or 72 per cent perchloric acid. This compound is a gas boiling at -15.9° and melting at -167.5°C . The compound is extremely reactive as is characteristic of all compounds containing an $\text{O}-\text{F}$ bond. It is explosive in all states. It always exploded on freezing or in the gas phase on contact with organic substances or with 2*M* potassium iodide solution. It reacts with aqueous iodide or base according to the equations:



To prevent explosions, these reactions were carried out by allowing the gas to diffuse slowly through air to the solution.

ORGANIC PERCHLORATES

Adducts of organic compounds with metal perchlorates such as the pyridine adducts and the benzene and toluene complexes with silver perchlorate were discussed in Chapter 4. This section will deal with purely organic perchlorates such as amine perchlorates, oxonium, carbonium and diazonium salts, esters and the newly reported perchloryl compounds. There have been hundreds of these perchlorates reported. No attempt at a comprehensive review of the literature will be made here but rather general properties and characteristics will be discussed. Burton and Praill¹⁸ have reviewed the literature on these compounds in some detail and present a good bibliography.

Amine Perchlorates

A great number of these compounds have been prepared. They are generally crystalline salts which are quite stable at ordinary temperatures and not very soluble in water. Hofmann and co-workers^{42, 43} prepared a number of these compounds and measured their solubilities, some of which are listed in Table 5.2. These compounds can be prepared by the reaction of perchloric acid with the corresponding amine or metathesis between the amine halide and the perchlorate of an alkali metal or silver. The conductances^{56, 63, 73} of several of these salts have been measured in organic solvents in which they are generally quite highly dissociated.

Spallino⁷² prepared the perchlorates of a number of aromatic amines

TABLE 5.2. SOLUBILITIES OF SOME AMINE PERCHLORATES IN WATER⁴³

Compound	Solubility (g/100 g H ₂ O)	Temp. (°C)
Trimethylammonium perchlorate	>20	17
Ethylenediamine diperchlorate	~100	17
Tetramethylammonium perchlorate	1.554	25
Tetraethylammonium perchlorate	2.392	17
Ethyltrimethylammonium perchlorate	11.97	20
Bromoethyltrimethylammonium perchlorate	3.59	19
Hydroxyethyltrimethylammonium perchlorate	0.89	20
Vinyltrimethylammonium perchlorate	5.764	20

by reacting the sulfate of the organic base with barium perchlorate in a minimum of water.

All of these compounds when heated slowly will either volatilize or decompose. However, if subjected suddenly to a high temperature they will explode. Datta and Chatterjee²² determined the minimum temperatures at which explosion would take place for a number of perchlorates. These compounds generally have explosion temperatures in the range 250 to 300°C; none exploded below 200°. Generally the explosion temperatures of perchlorates were considerably lower than those of the corresponding picrates or of the nitro compounds. These results are also discussed in Chapter 11.

The conductances, dissociation constants and thermodynamic constants of dissociation of a series of substituted phenyltrimethylammonium perchlorates were determined by Dennison and Ramsey²³ in ethylene chloride and ethylidene chloride. These salts were prepared by M. Bloom by metathesis between sodium perchlorate and the iodide of the base in 95 per cent ethanol. The melting points of the salts are shown in Table 5.3. Activity coefficients of tetrabutylammonium perchlorate and tetraphenylphosphonium perchlorate have been reported by Deno and Perizzolo.²⁴ The preparation and properties of the perchlorates of some alkanolamines was described by Cadle and co-workers.¹⁴

TABLE 5.3. MELTING POINTS OF SOME SUBSTITUTED
PHENYLTRIMETHYLAMMONIUM PERCHLORATES²³

Substituent and Position	M.P.	Substituent and Position	M.P.
<i>o</i> -Methyl	196.5	<i>p</i> -Methoxy	193.1
<i>m</i> -Methyl	123	<i>o</i> -Chloro	185.0
<i>p</i> -Methyl	202.5	<i>m</i> -Chloro	165.0
<i>o</i> -Methoxy	230.0	<i>p</i> -Chloro	225.7
<i>m</i> -Methoxy	153.2		

Diazonium Perchlorates

A number of diazonium perchlorates were prepared by Hofmann and Arnoldi.³⁹ These salts are sparingly soluble in water and are extremely explosive. The authors report that benzenediazonium perchlorate, a crystalline salt, is so explosive that a few centigrams of the compound, if allowed to fall on hard wood, will tear a deep hole in it. *o*-Toluenediazonium perchlorate will explode with great severity from the slightest pressure of a porcelain spatula, even when the compound is moist with ether. The α - and β -naphthalenediazonium perchlorates also exploded violently when dry. The diazonium perchlorate of *p*-phenylenediamine was reported in 1910 to be the most explosive substance known.⁴³ Their coupling power show them to be normal diazonium derivatives.

Oxonium and Carbonium Perchlorates

The arylmethyl perchlorates were among the first carbonium salts to be prepared.^{33, 34} They are readily formed by the action of perchloric acid on the corresponding carbinols or by metathesis of the chloride with silver perchlorate in a solvent such as nitrobenzene. The triarylmethyl perchlorates are highly colored crystalline materials of relatively high melting points.

The diarylmethyl perchlorates have not been investigated very extensively. Diphenylmethyl perchlorate, prepared *in situ* from diphenylmethyl chloride and silver perchlorate, converts benzene to triphenylmethane in good yield at room temperature.⁹

Benzyl perchlorate is an exceedingly reactive substance which rapidly polymerizes in solution unless it reacts with the solvent. It reacts rapidly with benzene or toluene to give high yields of diphenylmethane and *p*-methyldiphenylmethane, respectively.¹²

Perchloric acid forms oxonium or carbonium salts with a number of aldehydes, ketones and ethers. Hofmann and co-workers^{40, 41} described the perchlorates of diphenylketone, xanthone, carbazole, naphthazine and a number of others. These compounds can be crystallized from a number of nonaqueous solvents such as carbon tetrachloride and ethyl ether. The salts are all immediately decomposed by moisture. These authors suggest that concentrated perchloric acid may be used with advantage for the isolation and identification of many ketones and also of feebly basic nitrogen derivatives. The elimination of perchloric acid from its salts is easier than that of picric acid from picrates. The salts are generally somewhat less stable than amine perchlorates but more stable than the diazonium perchlorates.

Pfeiffer and co-workers⁶⁵ prepared and described the perchlorates of a number of aromatic ketones. These compounds are for the most part

rather unstable. Melting points were reported but in a number of cases these were given as a range of as much as 14°C. Gomberg and Cone³⁴ prepared and described a number of quinocarbonium perchlorates. Smeets⁷¹ reported obtaining a molecular compound of dioxane and perchloric acid by mixing dioxane with 70 per cent perchloric acid and immediately cooling the solution to 0°C. Needles of the reported composition $\text{HClO}_4 \cdot \text{H}_2\text{O} \cdot \text{C}_4\text{H}_8\text{O}_2$ separated from the solution. Analysis, however, show a ratio of 24:19:50. The melting point is reported to be 80 to 82°C. The compound is stable in a dry atmosphere, but liquefies in moist air.

Perchlorate Esters

Ethyl perchlorate was first prepared by Hare and Boye in 1841.³⁸ The compound is extremely explosive, being sensitive to both heat and shock. It is immiscible with water by which it is slowly hydrolyzed. It is soluble in alcohol and its solution in the latter when sufficiently dilute burns entirely away without explosion.

Meyer and Spormann⁶¹ prepared methyl, ethyl, and propyl perchlorates by the distillation of barium perchlorate with the corresponding alcohol. The methyl and ethyl esters could also be obtained by double decomposition of silver perchlorate with the alkyl halides or from anhydrous perchloric acid and the alcohol. The boiling point of methyl perchlorate is 52°C and that of ethyl perchlorate is 89°. The methyl ester was also prepared by methylating the anhydrous acid with diazomethane.

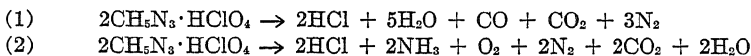
The kinetics of the reaction between silver perchlorate and methyl iodide was studied by Redies and Iredale⁶⁶ in a number of solvents. The energies of activation range from 11 to 13 kcal. The perchloric ester of epichlorohydrin, $\text{ClCH}_2\text{CH}(\text{OH})\text{CH}_2\text{ClO}_4$ and the glycol ester, $\text{HOC}_2\text{H}_4\text{OC}_2\text{H}_4\text{ClO}_4$ made from ethylene oxide were reported by Hofmann and co-workers.⁴⁵ These compounds are heavy, colorless, very hygroscopic oils which were reported to be much more explosive than nitroglycerin.

Trichloromethyl perchlorate, CCl_3ClO_4 , was prepared by Birckenbach and Goubeau⁶ and by Correns¹⁶ by reaction between carbon tetrachloride and silver perchlorate in the presence of a little hydrogen chloride. By repeated fractionation in a vacuum in the absence of moisture the product was obtained as a colorless liquid which solidified at about -55°C. It reacts with water yielding perchloric acid and liberates iodine from iodides. It detonates on contact with alcohol and other organic substances or upon heating.

Schmeisser⁶⁹ prepared acetyl perchlorate and benzoyl perchlorate by the reaction of silver perchlorate with the corresponding acid chlorides. The reactions of these compounds as acetylating and benzoylating agents have been studied by Burton and Praill.^{10, 11}

Guanidine Perchlorate

The thermal decomposition of this compound has been studied by Glasner and Makovsky.²⁸⁻³⁰ They prepared the compound from the chloride and sodium perchlorate. It has a melting point of 240°C. On heating at or below 300°C only a very slight loss of weight is observed after several hours. Above 400° ignition occurs after a definite induction period, with the formation of a yellow solid residue. In the range 300 to 400° the decomposition occurs at a measurable rate. Analyses of the gases formed indicate that the decomposition can be described by the equations:



Generally reaction 2 predominates with reaction 1 becoming more pronounced with increasing temperature. A rather complex mechanism is indicated with the intermediate formation of ammonia, perchloric acid, cyanamide and melamine. In the temperature range 320 to 390° the molten salt gradually changed into an unidentified waxy yellow solid before decomposing completely.

The over-all reaction appears to be zero order, with a rate constant $k = 2.4 \times 10^{11} e^{-32,400/RT}$ %/min. Catalysts for the decomposition have been studied and conditions under which guanidine perchlorate explodes or deflagrates have been defined.

Perchloryl Compounds

The compounds of this newly discovered class⁴⁷ are formed from a Friedel-Crafts type of reaction between perchloryl fluoride and aromatic compounds.

Perchloryl benzene ($\text{C}_6\text{H}_5\text{ClO}_3$) has been prepared by the reaction of benzene with perchloryl fluoride in the presence of aluminum chloride. This compound has a boiling point of 232°C and a freezing point of -3°. The density at 30° is 1.185.

Hydrolysis of perchloryl benzene with potassium hydroxide solution gave potassium chlorate and phenol. Nitration of the compound with a nitrating mixture of concentrated sulfuric and nitric acids give 3-nitroperchlorylbenzene as very pale yellow needles melting at 49 to 50°C. Alkaline hydrolysis of 3-nitroperchlorylbenzene gave 3-nitrophenol. The reaction of 3-nitroperchloryl benzene with hydrochloric acid and stannous chloride resulted in the formation of 3-aminoperchlorylbenzene, colorless needles, m.p. 30 to 31°C.

3-Perchlorylacetanilide, colorless needles, m.p. 136 to 137°C was prepared from 3-aminoperchlorylbenzene by acetylation in the usual manner with acetic anhydride and glacial acetic acid.

4-Fluoroperchlorylbenzene was prepared by the reaction of fluorobenzene with perchloryl fluoride in the presence of anhydrous aluminum chloride. The compound melts at 28°C and has a boiling point of 53° at 0.25 mm.

2,5-Dimethylperchlorylbenzene was prepared by perchlorylation of *p*-xylene. The compound was recrystallized from light petroleum ether as colorless needles, m.p. 30 to 31°C. It has a vapor pressure of 0.3 mm. at 85°.

These perchloryl aromatic compounds are comparatively stable, although sensitive to vigorous shock and high temperature.

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6. MANUFACTURE OF PERCHLORIC ACID AND PERCHLORATES

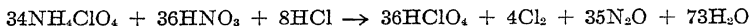
PERCHLORIC ACID

Possible Methods

Various methods for the commercial manufacture of perchloric acid have been proposed or used in the past, but these have been based mainly on the early work of von Stadion and of Serullas (see Chapter 1 on History).

One of the first commercial methods used was the vacuum distillation of the acid from a mixture of potassium perchlorate and sulfuric acid, as first carried out by von Stadion.⁷⁶ This procedure was somewhat difficult to use from the apparatus standpoint, and was later replaced⁸⁰ by the use of hydrofluosilicic acid, as first proposed by Serullas in 1831.⁷¹ By this method, insoluble potassium fluosilicate was precipitated and filtered off, leaving a dilute solution of perchloric acid which could be concentrated and vacuum distilled if desired. However, this method also was difficult to operate satisfactorily, primarily due to the gelatinous nature of the precipitate. Another somewhat similar method was proposed²⁸ using barium perchlorate and sulfuric acid, but in this case the barium salt was much too expensive for commercial use. Still another method—which was never used commercially—was that discovered by Serullas⁶⁹ in 1830; namely, the decomposition of aqueous chloric acid to perchloric acid by heat.

About 1925, a process previously proposed by Willard⁸⁸ was put into commercial use. This was based on the oxidation of ammonium perchlorate with a mixture of nitric and hydrochloric acids. The approximate over-all reaction may be represented as follows:



The resulting dilute solution of perchloric acid was then concentrated to a boiling point of 200°C, at which point it was free of any remaining hydrochloric or nitric acids. However, it was feared that this process involved a possible explosion hazard, and it is no longer used on any large scale.

Perchloric acid forms a constant boiling mixture at a concentration of 72.4 per cent, with a boiling point of 203°C. Small amounts of the anhydrous acid can be prepared by vacuum distillation at 8 to 18 mm Hg and a temperature of 110 to 120°C. According to Smith and Goehler,^{23, 74} this process can be made more efficient if sulfuric or phosphoric acid is added, and the resulting product is somewhat more stable. However, anhydrous perchloric acid is a very hazardous reagent at best, and should not be prepared except for immediate research use. Upon standing at room tempera-

ture, it gradually darkens in color from lemon-yellow through straw to brown, and finally explodes. Only at temperatures of liquid air can it be stored indefinitely.²³

I.C.C. regulations permit the shipment of perchloric acid up to 72 per cent concentration. For further information on the safe handling, shipping and storage of perchloric acid, see Chapter 11.

An electrolytic method of preparing perchloric acid by the anodic oxidation of HCl was patented by Walker in 1918⁸¹ and was further investigated by Goodwin and Walker.²⁴ They found, however, that only a very dilute HCl could be used, thus requiring considerable evaporation to concentrate the product. With 0.1*N* HCl, 50 per cent of the HCl went to HClO₄ and 50 per cent to Cl₂, while with 1*N* HCl, almost 100 per cent went to Cl₂. By operating in three stages, they were able to use 0.5*N* HCl with fair success, and this process was subsequently placed in commercial use by the Genesee Chemical Company of Batavia, New York.

Another electrolytic method, involving the anodic oxidation of a chlorate in a two-diaphragm, three-compartment cell, was studied by Newnam and Mathers.⁴⁸ This method, using a platinum anode and an iron cathode, gave an aqueous perchloric acid of about 2*N* which could then be concentrated to 70 per cent and vacuum-distilled if desired. However, these authors concluded that the sodium perchlorate-hydrochloric acid method, first proposed by Kreider³⁸ and later investigated by Mathers,⁴⁸ would be the most suitable process for commercial use. This latter method consisted in treating sodium perchlorate with strong HCl to precipitate most of the sodium as NaCl. The solution could then be evaporated to remove the excess HCl and to concentrate the liberated perchloric acid, which could be subsequently purified by vacuum distillation.

Pernert Process

The same general idea of reacting sodium perchlorate with HCl is the basis of the *Pernert Process*⁵³ which was patented in 1946, and which also includes a number of novel mechanical features to facilitate continuous operation and more or less automatic control. These are described in the patent in considerable detail.

This process is now used commercially for perchloric acid manufacture by Hooker Electrochemical Company of Niagara Falls, New York. It consists briefly of the following steps:

1. NaClO₄ is dissolved in water and reacted with an excess of concentrated HCl to precipitate NaCl.

2. The NaCl is filtered off to give a filtrate containing about 32 per cent HClO₄.

3. The excess HCl is then boiled off, condensed and returned to Step 1 as 35 per cent HCl, leaving a liquor containing about 39 per cent HClO₄.

4. This acid liquor is then concentrated by evaporation to about 57 per cent HClO_4 while any remaining HCl passes off in the vapors.

5. This crude perchloric acid is then vacuum distilled in glass or glass-lined apparatus to produce a product of 70 to 71 per cent HClO_4 of high purity, while crystals of residual NaClO_4 , which form in the still bottoms, are removed and returned to Step 1.

The unique features of this process include a novel arrangement of stills and condensers, and a method by which the NaClO_4 crystals are removed continuously in Step 5. This latter operation is carried out by gravity settling through a barometric column of liquor above an open-top receiver, or seal pot, from which the slurry passes to a filter for return of the solids to the start of the process.

PERCHLORATES

Various possible methods for the primary production of perchlorates are known, and although some of these may have no commercial significance, they are listed below for comparison and as subjects of possible interest to the reader.

1. Electrolytic conversion of a chlorate in aqueous solution to perchlorate by anodic oxidation.

2. Electrolytic oxidation of chloride to perchlorate.

3. Thermal decomposition of a chlorate to perchlorate, chloride and oxygen.

4. Neutralization of perchloric acid with the appropriate base, or with certain metals.

5. Direct chemical oxidation of chlorates to perchlorates by strong oxidizing agents, such as ozone, persulfates and lead dioxide.

6. Reaction of a strong mineral acid on a chlorate to produce perchlorate, chloride and chlorine dioxide.

7. Natural oxidation of chlorides.

Electrolytic Conversion of Chlorates to Perchlorates. The electrolytic method shown as No. 1 above is the only commercially important procedure now used for the manufacture of sodium perchlorate. However, this salt is seldom marketed as such but is used almost exclusively as an intermediate for the manufacture of other perchlorate products such as perchloric acid, as previously described, and the potassium, ammonium and lithium salts. These salts may all be made conveniently from sodium perchlorate by processes of metathesis, or double decomposition. Details of such procedures are discussed in subsequent sections of this chapter.

Historically, the development of the electrolytic method of preparing perchlorates has been discussed in Chapter 1. However, a brief outline of the more important advances in the technology of this process over the years is presented herewith in Table 6.1 for convenient reference.

TABLE 61.1. HISTORICAL DEVELOPMENT OF THE ELECTROCHEMICAL PERCHLORATE PROCESS

Adapted from—Pennsylvania Salt Manufacturing Co. Report, "Investigation of Methods to Produce Sodium Perchlorate without the Use of Platinum", Part I, Literature Review, Aug. 31, 1951, (Declassified) Contract No-NONR 372(00), Office of Naval Research. (With permission of Office of Naval Research).

Source/year (Ref.)	Electrolyte	Anode	Cathode	Temperature	Current density	pH	Voltage	Other observations
Forster/1898 (20)	KClO ₃ —5% soln. NaClO ₃ —up to 50% soln. Current yields increased with increasing electrolyte conc.	Pt	No reduction at Pt, Pb, Cu, Zn, or Ni at high C.D. but rapid reduction at Fe and Co.	Low temp. (17–20°C) very much better than high temp. (75°C). Intermediate temps. were not investigated.	Up to 16.6 amps/dm ² . Obtained up to 98% yield over 22 hr in electrolyzing a 50% soln. at a C.D. of 8.3 amps/dm ² .	Neutral or acid. In alk. soln., oxidation of chlorate occurs only at the beginning.	4.5 v	Theoretically, 1 amp should convert 50 g NaClO ₃ to NaClO ₄ in 25 hr. O ₂ observed toward end of run. Current yields with KClO ₃ were lower than with NaClO ₃ .
Winteler/1898 (85)	KClO ₃ —saturated soln.; NaClO ₃ —50% soln. gave about same results as 20% soln.; 5% soln. gave lower yields; apparently a minimum conc. exists above which conc. is without effect.	Pt (Platinized Pt is unsuitable.)	Pt	Should be below room temp. Poor yields obtained at 50–80°C. No oxidation observed at 100°C. (At boiling point, cathodic reduction occurred.)	Investigated 1, 4, 8, 16 amps/dm ² . Yield increases with increasing C.D.	Neutral	6 v with KClO ₃ , 4–4.5 v with NaClO ₃ .	Current yields with KClO ₃ are same when equiv. concns. are used. Some reduction occurs if cathode C.D. falls below 2 amps/dm ² . Mechanical agitation is essential.
Lederlin (Pats.) 1902–3 (39, 40, 41)	Proposes use of dichromate.	—	—	—	—	Nonalkaline conditions.	—	—
Oechel/1903 (51)	Used 4 to 66% NaClO ₃ solns. Stages use of Na ₂ Cr ₂ O ₇ (2 g/l) eliminates cathodic reduction.	Pt (glowed), 3 x 4 cm sheets. (Platinized Pt gave very much lower yields.)	Platinized Pt (one-sided sheets, one on either side of anode).	Low temp. gave best results. No perchlorate formed at 80°C, intermediate temps. not studied.	Used 2–3 amps/dm ² . If C.D. is high enough, chlorate conc. must fall below a very low value before current yield is appreciably affected.	Increasing alkalinity decreases current yields.	A minimum anode potential is necessary (value not stated).	Amount of O ₂ increases as electrolysis continues. Current yield is always a few % lower at start than later in process.

Allmand/1912 (2). (Reviewing commercial practice.)	NaClO ₂ —60 to 70% soln.	Smooth Pt. High over-voltage said to minimize OH ⁻ discharge.	Fe	Under 10°C.	8 amps/dm ²	Slightly acid.	6.5-7 v	Good agitation is needed. Current eff. averages 88%. 1 Kg NaClO ₄ requires 3.5 kwh.
German Pat./1919 (50)	KClO ₃ solutions.	—	—	27°C	15 amps/dm ²	—	—	—
Williams/1920 (84) (Reviewing commercial practice.)	NaClO ₂ —400 to 700 g/l.	Pt	Fe	Initially about 30°C (gradually rises to 45-50°C). Williams' own work showed current eff. does not fall off rapidly up to 60°C. The higher temps. give better current yields: Factor average 3.5 Williams at 42° 3.4 Williams at 59° 3.0	Initially 45-50 amps/dm ² (gradually falls to 30 amps/dm ²).	Should not be alkaline, but there is no advantage to acidifying except at higher temps.	Voltage increases as electrolysis proceeds.	O ₂ appears only after NaClO ₂ concn. falls below 10 g/l. Avg. current eff. is 85% or better. During electrolysis NaCl is produced and there is an equilibrium value for each temp. (2.3 g/l at 31° to 4.7 g/l at 55°).
Knibbs <i>et al.</i> /1920 (37)	Chlorate solns. show max. conductivity at 550-600 g/l; perchlorate solns. at 600 g/l. Conductivity falls off above this conc.	—	—	Conductivity increases with temp. Discusses effect of temp. on conc. and discharge of OH ⁻ , Cl ⁻ , ClO ⁻ and on other possible anode reactions.	—	Acidity needed to reduce loss of current thru OH ⁻ and Cl ⁻ discharge.	—	Total resistance of perchlorate cell is much higher at and than at beginning of electrolysis although electrolyte resistance may be the same.
Blau <i>et al.</i> /1921 (11)	KClO ₃ solutions—60 g/l	Pt	Ni	24-27°C Current yield decreased markedly as temp. increased above 20°C when low C.D. is used (10 amps/dm ²).	15 amps/dm ² (anode & cathode). Current yield mounted with increase in cathode C.D. while a change in anode C.D. had little effect.	—	7.4-8.5	KClO ₄ crusts anodes even with high electrolyte velocities.

Source/year (Ref.)	Electrolyte	Anode	Cathode	Temperature	Current density	pH	Voltage	Other observations
Ehrhardt (Pat.)/1932 (16)	NaClO ₂ —900 g/l at start. NaClO ₂ is added continuously as electrolysis pro- ceeds, not allowing it to drop below 150 g/l until NaClO ₂ is 1000 g/l.	Pt	Fe	40-50°C	38 ampere/dm ²	—	—	Current eff. = 98%. 1 Kg NaClO ₄ requires 3.0 KWH; Pt loss = 3 mg/Kg KClO ₄ .
Delavenna/1938 (14)	Solution kept satu- rated with NaClO ₂ .	—	—	0°C or lower	High C.D. not essen- tial if special cell is employed (very rapid circulation, pressure, cooling).	—	—	—
Ruis <i>et al.</i> /1944 (57)	Current eff. is propor- tional to chlorate conc.	Pt	—	—	Current eff. is pro- portional to $-\frac{3}{4}$ power of C.D.	—	—	—

Electrolytic Oxidation of Chlorides. Although a number of previous authors^{2, 52, 85} had observed various conditions under which small amounts of NaCl may be oxidized all the way to perchlorate in a chlorate cell, Kato *et al.*⁸⁵ studied the stepwise nature of this over-all reaction, but carried it out in a single cell with a lead dioxide anode. Starting with a saturated NaCl solution, they reported 98 per cent conversion of the chloride to perchlorate at 49 per cent current efficiency at 32°C with an expenditure of 17.9 kwh/kg of perchlorate.

The electrolytic conversion of alkaline earth chlorides to perchlorates appears to occur more readily than with the sodium or potassium salts which give relatively low yields. However, in the case of lithium, which has a small ionic radius and resembles magnesium in many of its reactions, the chloride is readily converted to perchlorate at high yield.^{31, 32} On the other hand, rubidium chloride cannot be electrolyzed beyond the chlorate state.³⁰

In the electrolysis of ammonium chloride, explosive NCl_3 appeared during the early stages, but at the end of the electrolysis all NH_4^+ had disappeared and the solution became strongly acid, with perchlorate ion present.³²

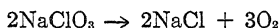
The electrolytic oxidation of a solution of sodium hypochlorite to perchlorate, using a lead dioxide anode, has been suggested⁷⁸ as another possible means of perchlorate manufacture, but at present only the two-stage electrolysis of sodium chloride via the chlorate as an intermediate (Method No. 1) is of commercial importance.

Thermal Decomposition of a Chlorate. The thermal decomposition, or "self-oxidation," of chloric acid to produce perchloric acid and that of potassium chlorate to produce potassium perchlorate were first observed by Serullas^{69, 71} in 1830 and 1831, respectively. However, the development of such a process for perchlorate manufacture does not appear to have ever reached the commercial stage, although a great deal of study has been devoted to the reactions involved, particularly in the case of the potassium salts. For example, the time-temperature relationships required for the optimum yield of KClO_4 have been determined by Blau and Weingand¹¹ and by Mathers and Aldred,⁴⁶ while other studies have been carried out by such authors as Sodeau,⁷⁵ Scobai,⁶⁸ Farmer and Firth,¹⁸ and Frankland and Dingwall.²¹

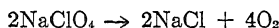
In the case of the sodium salts, the production of sodium perchlorate by the thermal decomposition of sodium chlorate has been patented by Schumacher.⁶⁴ This patent specifies the time-temperature requirements for heating NaClO_3 in order to obtain the optimum yield of perchlorate by way of the probable reaction:



while at the same time minimizing the complete decomposition of the chlorate and/or perchlorate by the possible reactions:



and



In carrying out the process, the sodium chlorate is melted and heated for a period of time in the temperature range of 400 to 600°C until the melt begins to thicken due to the formation of solid sodium perchlorate and sodium chloride, both of which have melting points above this range. The mass is then cooled and leached with a recycled liquor to dissolve out the perchlorate and remaining undecomposed chlorate, which are separated by a process of evaporation and fractional crystallization. The main portion of the sodium perchlorate is removed as product, while a crop of sodium chlorate, containing a small amount of perchlorate, is returned to the start of the process along with the make-up sodium chlorate being fed to the melter.

Under the most favorable conditions, only 3 moles of perchlorate are obtained for every 4 moles of chlorate decomposed. However, laboratory tests have indicated that much lower yields may be quite frequent due to the difficulties involved in establishing and maintaining optimum conditions. The catalytic effect of impurities may also have a marked effect upon the results, while the high temperatures involved present problems in regard to materials of construction. Thus, in view of the poor efficiency and the various difficulties presented, the thermal decomposition of chlorates does not appear attractive as a commercial means of manufacturing perchlorates.

Perchloric Acid Neutralization. Since perchloric acid is now also made almost exclusively from sodium perchlorate as already described, the neutralization of this acid with a base or with a metal, such as zinc or magnesium (Method No. 4 above), can hardly be regarded as an economical procedure for large scale perchlorate manufacture. However, it may be found useful as a convenient laboratory method for the preparation of small amounts of miscellaneous perchlorates, as pointed out later.

Chemical Oxidation Method. The reaction of strong oxidizing agents on chlorates for the production of perchlorates (Method No. 5), although not used commercially at the present time, is worthy of comment.

Under certain conditions, ozone will produce a small amount of perchlorate from chlorates, but much of the work thereon is inconclusive, and such a process is seemingly very inefficient. According to Bennett and Mack,⁹ a number of relatively strong oxidizing agents—e.g., potassium

permanganate and sodium peroxide—have no action on chlorates in aqueous solution, whereas a few others, such as sodium persulfate, will oxidize them to perchlorates. In this regard, Ehrhardt¹⁷ has reported that lead dioxide (PbO_2) in a strong sulfuric acid medium is very effective in producing perchlorates from chlorates with high yields. He gives considerable detail regarding such a process and discusses the possible methods of chemically regenerating the lead dioxide from the lead sulfate formed. This process was proposed for use in Germany during World War II; however, the economics involved in the regenerative operations would seemingly render the process unattractive from a present day commercial standpoint. Also, Schlachter⁵⁸ has predicted equipment difficulties with both the oxidation and the regeneration steps, but it is possible that new techniques may some day be found to revive interest in this process.

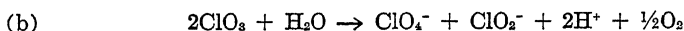
Other Methods. The reaction of strong mineral acids (Method No. 6) on chlorates gives very low yields.⁴² Therefore, it has little commercial importance as a method of producing perchlorates alone under present market conditions, but it is of value as a means of producing chlorine dioxide as a coproduct.²⁶

The mechanism by which small amounts of perchlorates are seemingly produced from chlorides by atmospheric oxidation in nature,⁷ as mentioned in Chapter 1, is as yet little understood. It may be due to some such effect as atmospheric oxidative weathering, photochemical processes or the action of microorganisms. However, as previously suggested, the further study of this phenomenon may possibly reveal new avenues of approach to perchlorate manufacture.

Sodium Perchlorate Manufacture: Electrochemical Process

Historically, the first production of perchlorates electrolytically was by von Stadion in 1816,⁷⁶ but it was not until 1895 that commercial manufacture using this method was commenced at Mansbo, Sweden.¹² One of the earliest publications of importance outlining the conditions for obtaining high current efficiency was by Foerster²⁰ in 1898 (see Chapter 1 on History).

There is still some question concerning the mechanism of the reaction involved in the electrochemical formation of perchlorates. Oechsli⁵¹ proposed the following set of reactions:

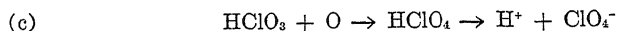
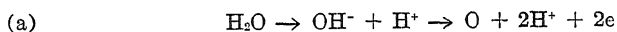


After discharge, ClO_3^- decomposes water, giving a mixture of per-

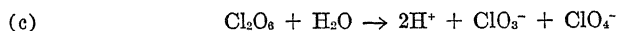
chlorate and chlorite with liberation of oxygen. The liberated oxygen then oxidizes the chlorite to chlorate, the total result being:



Bennett and Mack⁹ favored a theory of direct chemical oxidation by active oxygen. They argued that perchlorate is formed at the anode at a potential below that necessary for the continuous discharge of any ion present in the solution. A set of reactions corresponding to their theory is:



Knibbs and Palfreeman³⁷ supported Oechsli on the principle of chlorate ion discharge, but differed with him on the mechanism. They believed that the discharged ClO_3^- combined with another one to form Cl_2O_6 instead of reacting with water. This oxide immediately reacted with water to give chloric and perchloric acid. Thus, they proposed:



Knibbs and Palfreeman did not believe that the Bennett and Mack theory satisfactorily explained the variation of current efficiency with pH. According to either theory, it should be possible to produce one ion of perchlorate from one ion of chlorate by using two faradays of electrical energy at 100 per cent current efficiency.

Perchlorate Cell. Many perchlorate cells have been described in the literature. Detailed information on only three modern cells is available, plus a recent patent to Pennsalt Chemical Corporation,³³ a new producer of perchlorate.

The construction of the Schumacher cell used by American Potash & Chemical Corporation⁶⁰⁻⁶³ and the Cardox Corporation cell²⁷ are shown in Figures 6.1 and 6.2. All of the commercial cells have much in common, as is indicated (Table 6.2) by the characteristics of the I.G. Farben, (Bitterfeld) cell,^{44, 79} the Schumacher cell, and the Cardox Corporation cell.

Anode. Regardless of the mechanism at the electrodes in a perchlorate cell, it has been well established that a high anodic potential is essential. To secure this high potential, a smooth platinum electrode is generally used. In general, the classic literature, contains references to the use of platinum anodes. In this early work, the problem of cost was not involved and the characteristics of platinum dictated its use.

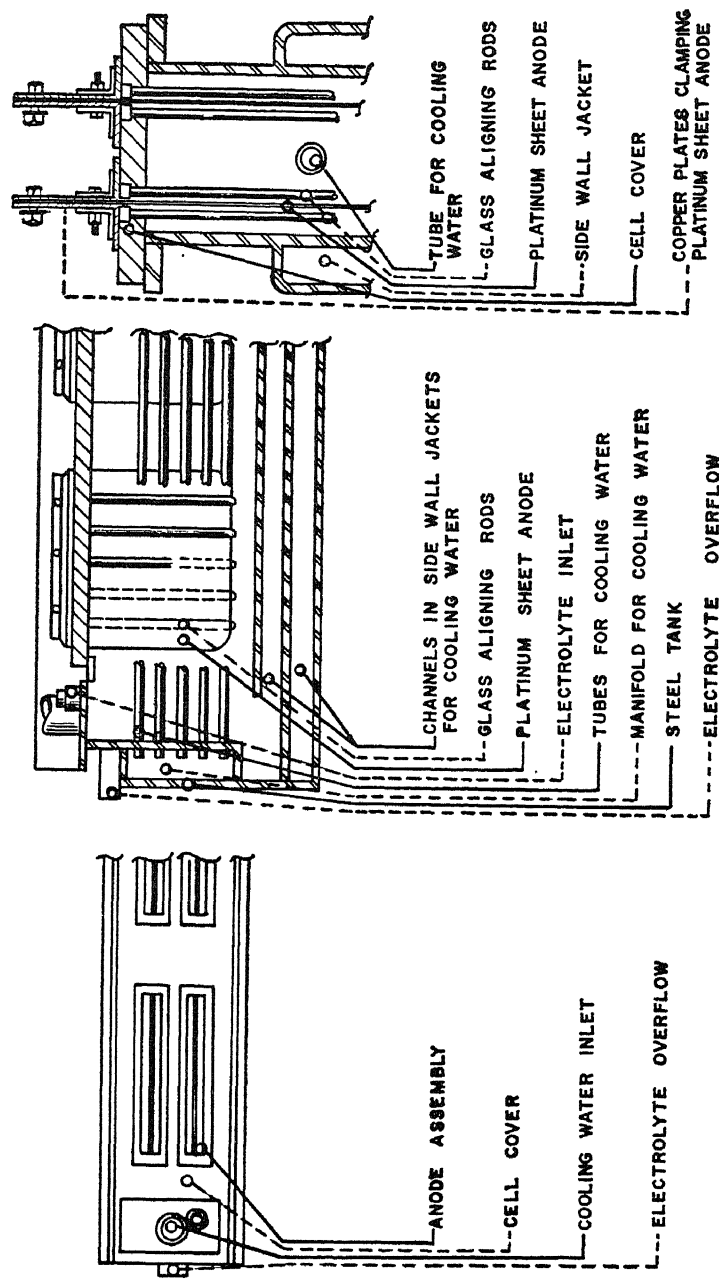


Figure 6.1. The Schumacher perchlorate cell.

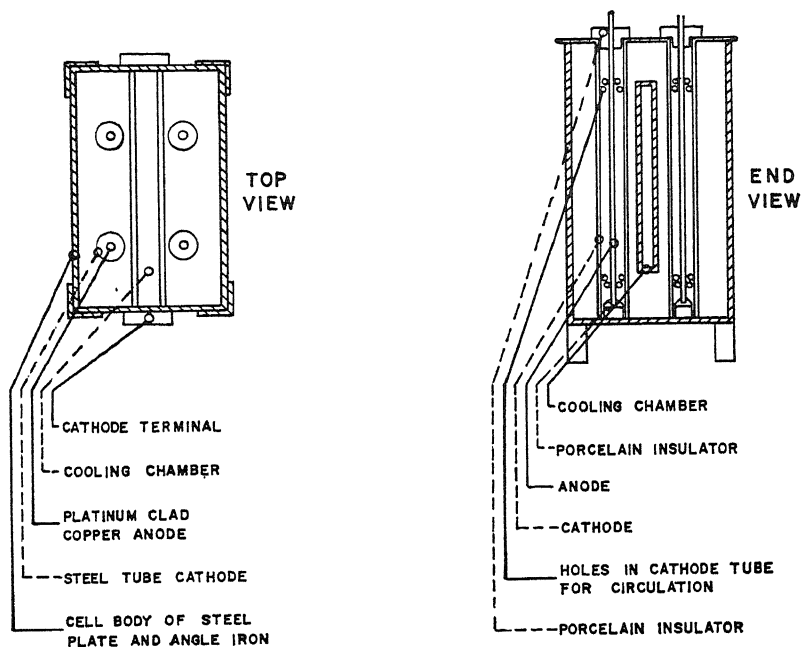


Figure 6.2. Cardox Corporation perchlorate cell.

In spite of its high cost and the corrosion and erosion that takes place in a cell when it is used as an anode, platinum is the material of choice for commercial cells. Solid, smooth platinum anodes were used by the early investigators. If a platinized anode is used, oxygen is evolved and the perchlorate yield falls. Two of the commercial cells previously discussed use solid, smooth platinum anodes. A list of the desirable characteristics of a platinum anode are given by Schumacher⁶¹:

1. The fabricated anode must possess good electrical characteristics.
2. It should have good mechanical strength.
3. It should have a high surface to weight ratio.
4. The fabrication cost should be low.
5. It should be easily removable from the cell for inspection and weighing.

Because of the high cost of platinum, it is desirable to use as little as necessary in the cell anode. Logically, a platinum cladding would decrease the amount of platinum used and the costs. The Cardox Corporation cell uses platinum-clad copper rods. The Pennsalt cell,³³ conceivably, takes advantage of Baum's work⁸ on platinum-coated tantalum as anodes for persulfate cells and uses platinum-clad tantalum anodes.

The search for a substitute for platinum started almost as soon as it became the anode of choice. Many materials have been considered:

TABLE 6.2. CELL CHARACTERISTICS ON COMMERCIAL
ELECTROLYTIC PERCHLORATE PRODUCTION

Anode	Material of construction	Size	No./cell	Loss ton of product
Cardox Corporation	Platinum-clad copper rods	0.5" (dia) x 30"	4	—
I. G. Farben, A. G. (Bitterfeld)	Platinum sheet	21.6" x 9.8" x 0.002"	16	0.1 Troy oz
American Potash & Chemical Corp.				
1st Phase	Platinum sheet (perforated)	14" x 16" x 0.006"	8	0.2 Troy oz
2nd Phase	Platinum sheet (perforated)	14" x 16" x 0.006"	8	0.2 Troy oz

Cathode	Material of construction	Size	Anode-cathode spacing
Cardox Corporation	Steel tubes	3" (dia) x 33" (4 tubes, each drilled with 8 to 10, $\frac{1}{2}$ " holes)	1.25 in.
I. G. Farben, A. G. (Bitterfeld)	Perforated steel plates (one on each side of anode)		1 cm
American Potash & Chemical Corp.			
1st Phase	Mild steel	Cell body	—
2nd Phase	Mild steel	Cell body	—

Cell body	Material of construction	Size	Capacity (cu ft)	Cover
Cardox Corporation	Sheet steel	30" x 16" x 33"	6.7	—
I. G. Farben, A. G. (Bitterfeld)	Steel with acid proof brick and coating	10' x 4' x 6.5'	(194 = 5.5m ³)	—
American Potash & Chemical Corp.				
1st Phase	Mild steel	8'6" x 5" x 2'0"	5.9	Synthetic stone
2nd Phase	Mild steel	6'6" x 5" x 2'0"	5.9	—

tungsten and molybdenum by Angel⁴; graphite by Ullmann⁸⁰ and Sihvon⁷²; silicon by Schoch and Pritchett⁵⁹; magnetite by Ullmann⁸⁰; manganese dioxide by Howard²⁹; and lead dioxide. Only the last material, lead dioxide, has proved of value in the manufacture of sodium perchlo-

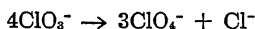
rate. In 1934, Angel and Mellquist⁵ reported that perchlorates could be produced using lead dioxide anodes. They found that the current efficiency increased with anode current density to a maximum of 79.2 per cent at a current density of 20 amps/dm² at 15°C. Also in 1934, Kato and Koizumi³⁴ produced perchlorate with lead dioxide anodes, with a 58 per cent current efficiency. Kitahara and Ohsuga³⁶ were able to increase the current efficiency in the preparation of perchlorate using lead dioxide anodes from 41 per cent to 70 per cent by the addition of sodium fluoride to the electrolyte.

Grigger *et al.*²⁵ obtained excellent conversions of chlorate to perchlorate using a lead dioxide anode. This was confirmed by Schumacher *et al.*⁶⁷ An industrial cell for the production of perchlorates, using lead dioxide anodes, has been described by Robertson and Hoffmann.⁵⁶

Cathode. The cathode in most perchlorate cells is mild steel which is generally the material of construction of the cell. The economic reasons for using mild steel are obvious. The steel is protected by the chromate ion added to the electrolyte. The reduction of chlorate or hypochlorite at the cathode to form chlorides is prevented by the presence of the chromate, which forms a protective film on the cathode.

Angel and Mellquist⁵ found that chromates were incompatible with lead dioxide anodes in the preparation of perchlorates. This was later verified by other workers.^{25, 56, 67} Without the chromate ion to coat and protect it, mild steel is not an acceptable cathode. Thus, nickel, stainless steel, and "Chem-Nickel"⁷⁷ are used as materials of construction for the cathode in a perchlorate electrolytic cell using lead dioxide anodes.

Electrolyte. The electrolyte fed to perchlorate cells generally contains sodium chlorate, sodium perchlorate, sodium chromate, sodium chloride, and sometimes sodium sulfate, calcium chloride, and magnesium chloride. The exact composition of the electrolyte depends on the operating conditions of the cells. If the operation is batch, then the cell feed contains a high concentration of sodium chlorate (500 to 600 g/l.). The cell feed also contains some sodium perchlorate because of the desirability of recycling mother liquor for the isolation of the sodium perchlorate. The concentration of chromate appears to depend on the operator of the cell; literature reports vary from 0.5 g/l. to 5.0 g/l. The sodium chloride in the cell feed may be introduced as an impurity in the sodium chlorate, or it may be introduced with the mother liquor from the sodium perchlorate isolation. Knibbs and Palfreeman³⁷ found that chloride ion concentration is established at a constant level, depending upon the temperature. If pure sodium chlorate is used, the chloride appears to be formed from the disproportionation of chlorate:



If sodium sulfate is present in the cell feed, it is because of its presence in the sodium chlorate as an impurity.

Calcium chloride and/or magnesium chloride are added to the cell feed to increase the current efficiency by decreasing the reduction of chlorate or hypochlorite ions at the cathode.

In the continuous process⁶⁰ the cell feed contains a higher concentration of sodium perchlorate. A typical cell feed in the continuous process would be 400 g/l. NaClO_4 , 400 g/l. NaClO_3 , and 5 g/l. $\text{Na}_2\text{Cr}_2\text{O}_7$.

Operation Considerations. The temperature of the electrolyte has an effect on current density, energy requirements, platinum loss, and cell efficiency. The earlier perchlorate cells were operated at low temperatures (10 to 30°C), while the modern cells are operated at higher temperatures (40 to 60°C). Williams⁵⁴ indicates that the over-all current efficiency varies very little with temperatures up to 60°C, while Knibbs and Palfreeman³⁷ obtained a 93 per cent current efficiency at 30°C and 83 per cent current efficiency at 60°C. The voltage drop across the cell decreases with increase in temperature. Williams obtained 6.5 v at 30°C and 5 v at 60°C. Knibbs and Palfreeman obtained roughly the same results, 6.45 v at 30°C and 5.26 v at 60°C. The energy requirements per pound of perchlorate produced depend directly on the current efficiency and the voltage drop across the cell. If the current efficiency is independent of temperature, then the higher temperature would give the lowest energy requirement per pound of perchlorate produced.

The platinum loss increases with temperature in the range of 40 to 65°C.⁶¹

From the previous discussion, it is apparent that the operating temperature of a perchlorate cell is a compromise. Generally, commercial cells are operated in the range of 35 to 50°C.

The circulation rate of the solution through the cell will vary with the operating conditions within the cell. In all perchlorate cells, it is necessary to remove heat to hold the temperature in the desired range. Most commercial cells have cooling coils as part of the cell body which also may be the cathode of the cell. More rapid circulation of the solution in the cell increases the heat transfer from the cell. In general, high current densities, low operating temperatures (<30°C), and low sodium chloride concentration (<100 g/l.) favor high circulation rates; the reverse is also true.

Even in the earliest experiments, the electrolysis of sodium chlorate was carried out in neutral or slightly acid solution. The solution is kept neutral or slightly acid to hinder OH^- discharge. Lederlin⁴⁰ obtained a patent covering the maintenance of nonalkaline conditions in a perchlorate cell. Knibbs and Palfreeman³⁷ favored keeping the hydroxyl ion concentration low, thus minimizing its discharge and its effect on current

density. Williams⁸⁴ pointed out the advantages of frequent addition of acid when operating at high temperature (40 to 60°C), but felt that acid addition was not necessary at low temperature. The commercial perchlorate cells operate at slightly acidic conditions, pH 6.6 to 6.8.

The current efficiency in a sodium perchlorate cell using smooth platinum anodes, containing sodium chlorate in concentrations above 100 g/l., is 90 per cent or better. Ehrhardt¹⁶ reported current efficiencies of 95 per cent. Williams⁸⁴ reported current efficiencies of 85 per cent. Knibbs and Palfreeman³⁷ found that the current efficiency increased with decreasing temperature. They found 93 per cent current efficiency at 30°C and 83 per cent current efficiency at 60°C. Schumacher⁶¹ reported 90 per cent current efficiency when the chlorate concentration was above 90 to 100 g/l. and 70 per cent current efficiency when the chlorate concentration was between 90 and 5 g/l. In general, the current efficiency drops rapidly after the sodium chlorate concentration is below 100 g/l. Near the end of the electrolysis, ozone is observed,^{20, 51, 84} and with the formation of ozone, the current efficiency is decreased.

Recent publications^{25, 67} indicate that high current efficiencies (above 90 per cent) can be obtained using lead dioxide anodes in the manufacture of sodium perchlorate.

The conversion of chlorate to perchlorate, for all practical purposes, is quantitative. Some chlorate may be lost by decomposition if the pH adjustment is made too rapidly with undiluted hydrochloric acid. The chloride in the form of hydrochloric acid is converted to chlorate, and then to perchlorate. Thus, for true conversion in the cell, both the sodium chlorate and sodium chloride in the feed solution, plus the hydrochloric acid used for pH adjustment, must be considered as starting materials for the perchlorate formed in the cell.

The economics of producing sodium perchlorate depends, in part, on the platinum lost in the cell. This loss occurs by two different methods: namely, chemical corrosion and erosion. Probably, the former is more important than the latter. Although all the platinum consumed by chemical corrosion does not necessarily occur as soluble platinum in the cell effluent, some may occur in the sludge from the cell. It is logical to assume that the chemical corrosion occurs at the platinum grain boundaries where the concentration of impurities is the highest. As the material at the grain boundaries is consumed chemically, the support for the platinum grain is removed and the solid platinum grain falls into the sludge. Schumacher⁶¹ reported 0.2 troy oz/ton of sodium perchlorate produced while the Bitterfeld, I. G. Farben plant reported 3 g (0.1 troy oz)/ton of potassium perchlorate.^{16, 79} Heitman, in U. S. Patent No. 2,825,643, claimed 91.9 per cent recovery of the platinum lost in a sodium perchlorate cell.

Considering the importance and expense of platinum in the manufacture

of sodium perchlorate, very little has been published on the exact effect of cell operating conditions on platinum loss. Schumacher⁶¹ reported increased platinum loss with increase in cell temperature from 40 to 65°C. He also reported increased platinum loss with an increase of current density from the range 2 to 3 amps/sq in. (31 to 46 amps/dm²).

Philipp and Morgan⁵⁴ made a brief study of the platinum loss with changing chloride concentration and found an increase in platinum loss with increased chloride concentration in the cell feed.

The voltage drop across a sodium perchlorate cell is made up of a large number of small voltage drops. Four of the important contributing factors to the over-all voltage drop are the anode-cathode spacing, the type and concentration of salts in the electrolyte, the current density on the anode, and the cell temperature. In general, the voltage drop across the cell is increased by: (a) increased anode-cathode distance; (b) high concentration of perchlorate ion and low concentration of chlorate ion; (c) higher current densities on the anode; (d) lower temperatures. In addition, the resistance drop in the anode, the resistance in the connection of the anode to the bus bar, and the condition of the cathode contribute to the over-all voltage drop across the cell.

The voltage drop in small laboratory cells is generally lower than production cells because of the closer anode-cathode spacing that is possible. Laboratory cells may have a voltage drop of 5.0 to 6.0 v, compared to 6.5 to 7.0 v for a plant operating cell.

The energy requirement, at the cell, for the production of sodium perchlorate is directly related to the voltage drop across the cell and the current efficiency. Ehrhardt¹⁸ reported that 1 kg of sodium perchlorate required 3.0 kwh, while Allmand² indicated 3.5 kwh/kg. Schumacher⁶¹ reports that 2.0 kwh (a.c.) are required per pound, or 4.4 kwh/kg of sodium perchlorate; this amount includes the auxiliary equipment in the process, such as fans, pumps, centrifugal, etc. It is obvious that design of the sodium perchlorate cell and the choice of operating conditions have a direct bearing on the energy requirements.

As indicated in Table 6.3, the operating conditions followed in commercial cells are a compromise based on the design of the cell and the type of anode used in the cell.

The methods of isolation of sodium perchlorate employed by American Potash & Chemical Corporation,⁶⁰⁻⁶³ Cardox Corporation,²⁷ and I. G. Farbenindustrie, A. G. (Bitterfeld)^{44,79} are sketched in Figures 6.3, 6.4 and 6.5.

Potassium Perchlorate Manufacture

Potassium perchlorate can be prepared in an electrolytic cell in a manner similar to the preparation of sodium perchlorate. However, in practice,

TABLE 6.3. OPERATING CONDITIONS IN COMMERCIAL
ELECTROLYTIC PERCHLORATE PRODUCTION

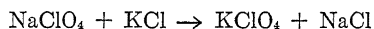
	Product	Raw material		
American Potash & Chemical Corp. 1st Phase 2nd Phase	$\text{NaClO}_3 + \text{NaClO}_4$ NaClO_4	NaClO_3 $\text{NaClO}_3 + \text{NaClO}_4$		
Charge	Initial conc. NaClO_3 (g/l)	Initial conc. $\text{Na}_2\text{Cr}_2\text{O}_7$ (g/l)	pH	
Cardox Corporation I. G. Farben, A. G. (Bitterfeld)	650-700 400-500 (more added periodically)	1 3-4	Alk., <10.5 Weakly acid	
American Potash & Chemical Corp. 1st Phase 2nd Phase	600 90-110 (+500 g NaClO_4 /l)	5 5	6.1-6.4 —	
Product	Final conc. NaClO_4 (g/l)	Final conc. NaClO_3 (g/l)		
Cardox Corporation I. G. Farben, A. G. (Bitterfeld) American Potash & Chemical Corp. 1st Phase 2nd Phase	800 1000 500 580-600	20 50 or less 90-110 5		
Electrical conditions	Current/ Cell (amps)	Current density (amps sq ft)		
		At anode	At cathode	
Cardox Corporation I. G. Farben, A. G. (Bitterfeld) American Potash & Chemical Corp. 1st Phase 2nd Phase	500 12,000 5000 5000	480 (52 amp/dm ²) 279 (30.0 amp/dm ²) 288 (31.1 amp/dm ²) 288 (31.1 amp/dm ²)	— — 72 (7.7 amp/dm ²) 72 (7.7 amp/dm ²)	
Electrical conditions	Voltage per cell	Energy consumed	Energy efficiency	Current efficiency
Cardox Corporation I. G. Farben, A. G. (Bitterfeld) American Potash & Chemical Corp. 1st Phase 2nd Phase	6.2-6.8 6.5 6.8 6.8	1.6 kwh/lb 1.84 kwh/lb 1.5 kwh/lb 1.9 kwh/lb	— — 14.4% 11.4%	97% — 90% 70%

TABLE 6.3—*Continued.*

Miscellaneous	Operation	Pt loss (troy oz/ ton)	Temp (°C)	Production
Cardox Corporation	Batch	—	45-55	2 lb/cell/hr
I. G. Farben, A. G. (Bitterfeld)	Batch (8 days) with recirculation thru 5 cells in series.	0.1	35	83 tons/mo. (5 cells)
American Potash & Chemical Corp.				
1st Phase	Continuous, with recirculation at 2 gal./min thru cells in parallel.	0.2	40-45	
2nd Phase	Batch with recirculation at 2 gal./min.	0.2	40-45	

this method is not used because of the limited solubility of potassium perchlorate compared to sodium perchlorate. Crusting of the anodes is encountered in potassium perchlorate cells, even with high electrolyte velocities.¹¹ Foerster²⁰ reported lower current yields with potassium chlorate than with sodium chlorate.

Potassium perchlorate is manufactured by taking advantage of its lower solubility. Sodium perchlorate is reacted with a slight excess of potassium chloride, which results in the double decomposition reaction, forming potassium perchlorate and sodium chloride:



This latter is the stable salt pair through the normal range of temperatures. Therefore, the mutual solubility relations of these two salts may be expressed in terms of the internal ternary system,



as shown diagrammatically in Figure 6.6.

The reaction is carried out hot and a crop of solid sodium chloride is removed. The solution is then cooled to crystallize the potassium perchlorate. By controlling the rate of cooling, the potassium perchlorate crystal size and size distribution can be controlled. The potassium perchlorate is separated and washed in a centrifuge and is discharged directly into a continuous dryer.⁶²

In principle at least, the process of separating these two salts is similar to that subsequently described in detail for the separation of ammonium perchlorate and sodium chloride.

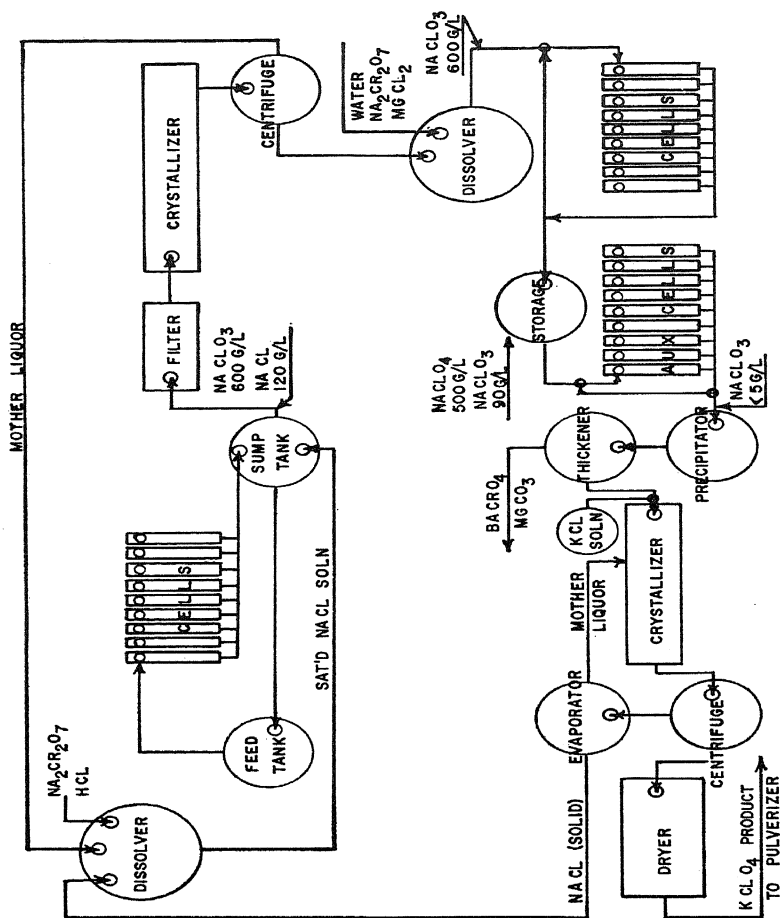


Figure 6.3. Isolation of sodium perchlorate, American Potash & Chemical Corporation.

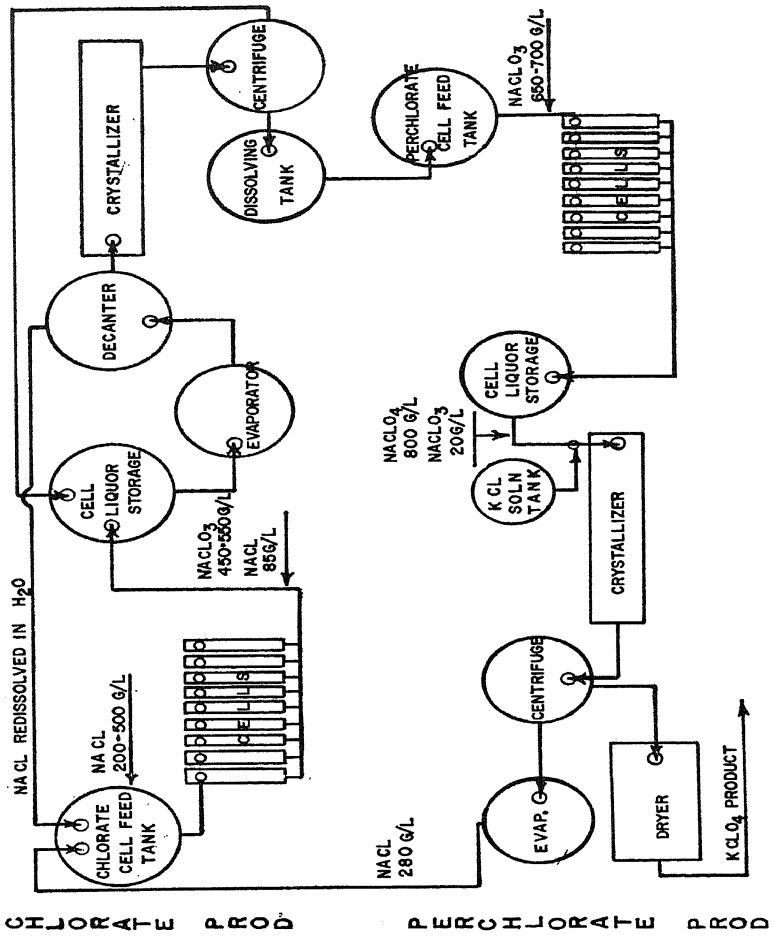


Figure 6.4. Isolation of sodium perchlorate, Cardox Corporation.

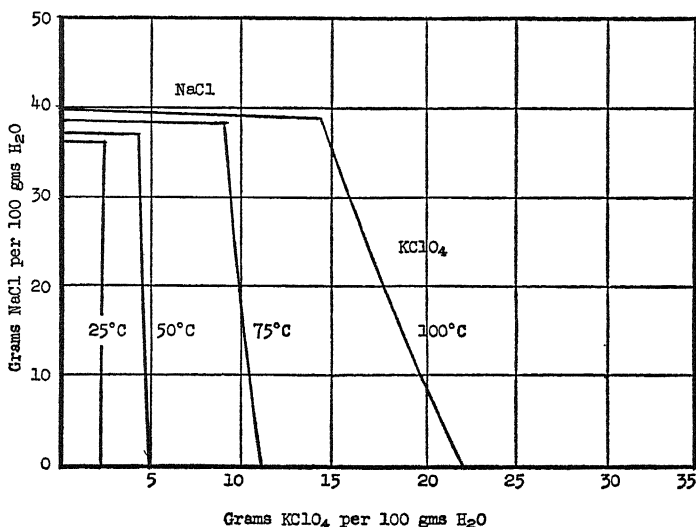
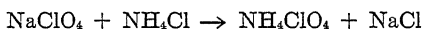


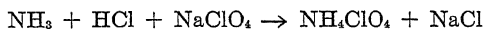
Figure 6.6. Mutual solubility relations for the system potassium perchlorate-sodium chloride-water. (Data from Cornec and Neumeister; *Caliche*, **10**, 492-4, 1929)

Ammonium Perchlorate Manufacture

In the commercial manufacture of ammonium perchlorate, sodium perchlorate is used as the starting material, with the ammonium ion being contributed by such materials as ammonium chloride, ammonium sulfate, or ammonium nitrate.^{1, 3, 13, 43, 62} The process on which the Western Electrochemical Company (now American Potash & Chemical Corporation) plant at Henderson, Nevada originally operated was based on the metathetical reaction of sodium perchlorate and ammonium chloride:



A modification of this reaction was developed by Schumacher^{6, 65, 66} which eliminated the production of ammonium chloride by reacting the sodium perchlorate with anhydrous ammonia and hydrochloric acid:



The feasibility of the process lies in the mutual solubility relationship between ammonium perchlorate and sodium chloride, which permits the reaction products to be separated by fractional crystallization. This relationship is plotted in Figure 6.7 for three temperatures. The mutual solubility of sodium chloride varies only slightly with temperature, while that of ammonium perchlorate is temperature-dependent. Thus, a saturated solution can be cooled with very little sodium chloride precipitating as contaminant. Further, by addition of a small quantity of water to the solution,

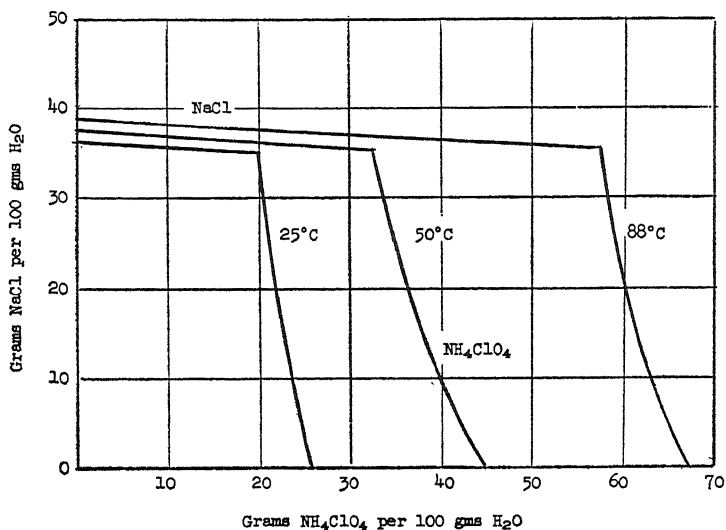


Figure 6.7. Mutual solubility relations for the system ammonium perchlorate-sodium chloride-water. (Schumacher and Stern, Ref. 66)

the system can be saturated with respect to ammonium perchlorate and undersaturated with respect to sodium chloride. Cooling of this system yields pure crystals of ammonium perchlorate.

The process is continuous and consists of six principal operations:

1. Reaction of ammonia, hydrochloric acid, and sodium perchlorate.
2. Fractional crystallization of ammonium perchlorate.
3. Centrifugation of the ammonium perchlorate.
4. Fractional crystallization of by-product sodium chloride.
5. Centrifugation of sodium chloride.

6. Drying, screening, blending, and packaging of the ammonium perchlorate product.

A simplified diagram of the process flow is presented in Figure 6.8.

Reactor System. The reaction takes place in a double-reactor system. The primary reactor is a 1000-gal., glass-lined, steam-jacketed vessel. Here, anhydrous ammonia, 31.8 per cent hydrochloric acid, and 56 per cent sodium perchlorate solution are reacted under atmospheric pressure at a temperature of 170°F with mild agitation. Approximately 25 per cent of the heat requirement is derived from the exothermic reaction of ammonia and hydrochloric acid. Also added to this reactor is recycle liquor from the sodium chloride mother liquor tank. This solution contains approximately 30 per cent ammonium perchlorate and 15 per cent sodium chloride. In addition, a small amount of treated water is fed to the reactor to insure undersaturation of the reaction mixture.

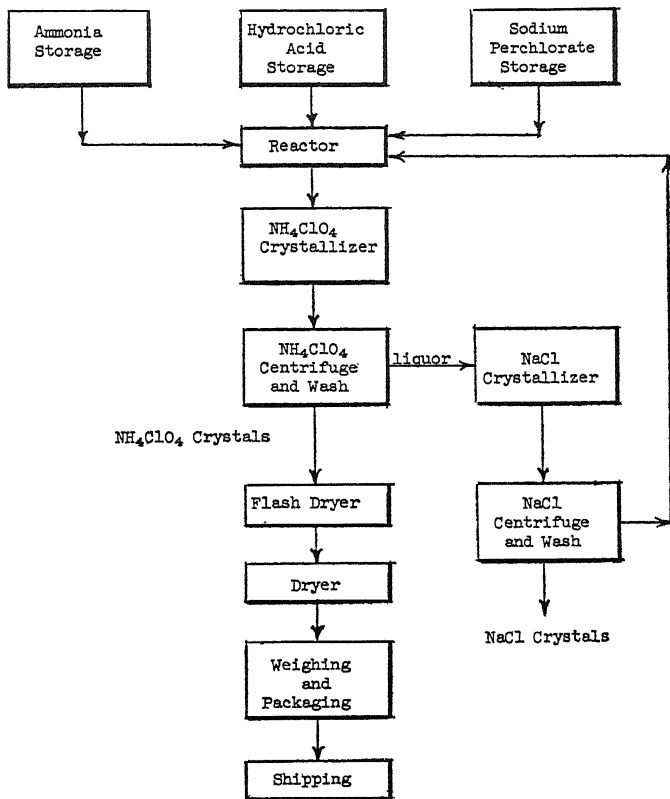


Figure 6.8. Simplified flow diagram of ammonium perchlorate manufacture.

After an approximately 30-min reaction period, the contents of the reactor, at a pH of 5.5, are fed into a 750-gal., glass-lined, steam-jacketed control tank. The purpose of this tank is to insure that the feed stream to the crystallizers will be of uniform composition.

The entire reaction system, as well as the crystallizer control panel, is continuously monitored from a centrally located console control panel. The reaction tank discharge pH is adjusted by automatic reset of the hydrochloric acid flow rate within narrow limits. The control tank discharge pH is monitored by injections of a secondary ammonia stream. In the event of a low pH, all feed streams to the reaction tank are shut off and the reactor charge is automatically recycled until the pH is corrected either manually or automatically. In the event of high pH, no recycle takes place and the adjustment must be made manually.

Ammonium Perchlorate Crystallization. A stream of mother liquor, containing 15 per cent sodium chloride and 30 per cent ammonium per-

chlorate, is continuously removed from the control tank and transferred to the crystallizer, where it mixes with a large amount of circulating mother liquor. The mixture is cooled by flashing off a portion of the water in the vaporizer section of the crystallizer. It then passes through a suspended bed of crystals, releasing its supersaturation and causing the crystals to grow. The desaturated liquor is again mixed with liquor from the control tank. The crystal formation process is extremely important. Crystal size distribution, as well as quality, is controlled by varying the degree of supersaturation, recirculation rate, temperature of crystallization, and crystal bed depth. The degree of supersaturation of the recirculating liquor is kept within the metastable field to minimize spontaneous formation of new crystals. The classifying action of the circulation solution permits only the largest crystals to settle to the bottom.

Ammonium Perchlorate Centrifugation. A slurry of finished crystals consisting of 40 per cent ammonium perchlorate crystals, 10 per cent ammonium perchlorate in solution, and 13 per cent sodium chloride, is withdrawn continuously from the crystallizer at a temperature of 109°F and transferred to the centrifuge. Prior to entering the centrifuge, the slurry passes through a centrifuge feeder where it is further concentrated, thereby substantially reducing the load to the centrifuge. The slurry is centrifuged to remove remaining mother liquor, washed with treated water, spin-dried, and discharged continuously into a reslurry tank. This operation produces a steady flow of ammonium perchlorate crystals which have a moisture content of approximately 5 per cent. The washed crystals are discharged directly into a tank of saturated ammonium perchlorate solution. This serves both to reduce the chloride concentration of the solids and as a transfer medium for the ammonium perchlorate to the drying operation.

Sodium Chloride Crystallization. The next step involves recovering the sodium chloride from the mother liquor wash tank, into which has been discharged the wash water and mother liquor from the ammonium perchlorate crystallizer and centrifuge.

Feed from the mother liquor tank is mixed continuously with the sodium chloride saturated solution in the circulation line of the sodium chloride crystallizer, which is similar in operation to the ammonium perchlorate crystallizer. Prior to entering the evaporator section of this crystallizer, the mixture is heated in a steam heat exchanger. Sodium chloride is crystallized at a temperature of 170°F by evaporation of approximately 20 per cent of the water in the feed liquor. In contrast to the ammonium perchlorate, little attention is paid to crystal growth other than to secure a particle size which will centrifuge and wash easily.

Sodium Chloride Centrifugation. The sodium chloride slurry from

the crystallizer is preconcentrated in the centrifuge feeder in preparation for centrifugation. The slurry is centrifuged, washed with water, and spun dry. Crystals containing 0.01 per cent sodium chlorate and 0.90 per cent sodium perchlorate as impurities are discharged to the sodium chloride dissolving tank. By-product sodium chloride is recovered. Mother liquor and wash water from the centrifuge unit, as well as a portion of the liquor from the second stage retention tank, are collected in the sodium chloride mother liquor tank. As mentioned before, this composite liquor, which contains 15 per cent sodium chloride and 30 per cent ammonium perchlorate, is returned to the reactor tank, completing the cycle. In the meantime, wet crystals from the ammonium perchlorate centrifuge are washed by reslurrying in an ammonium perchlorate saturated solution recycled from the drying and packaging operations.

Ammonium Perchlorate Drying and Packaging. Because of the potentially hazardous nature of the final drying, these last stages of the process are carried out in a separate building especially designed to insure safe operation.

The ammonium perchlorate slurry, containing 25 per cent ammonium perchlorate crystals and 19 per cent ammonium perchlorate in solution, is pumped to the second stage centrifuge feeder in the drying and packaging building. Excess mother liquor overflows at the top of the feeder and is piped by gravity to the second stage mother liquor accumulator tank.

The feeder discharge, heavily loaded with ammonium perchlorate crystals, is fed through a flexible pipe to the second stage centrifuge. The mother liquor discharges to the mother liquor accumulator tank while the wash water is sent to a fines dissolving tank.

The crystal cake is conveyed to a flash dryer, where a heated air stream (284°F) flashes off the surface moisture to a value of approximately 0.5 weight per cent. The purpose of the flash dryer is to reduce agglomeration and pan sticking in the tunnel dryer. Dust-laden air from the flash dryer is exhausted to a wet scrubber, and the scrubber solution is collected and discharged periodically to a fines dissolving tank.

Next, the ammonium perchlorate crystals are discharged at approximately 212°F by a gravity chute to a tunnel dryer. There the moisture content is reduced to less than 0.02 per cent. To distribute the crystals evenly across the dryer, a vibrating spreader feeder is used. The crystals are conveyed along the dryer by a vibrating motion of the dryer pans. The amplitude of the vibration is electronically controlled so that bed thickness and residence time may be varied. Moisture removal is effected by feeding air, heated to 284°F, through closed chambers directly beneath the dryer plates. A countercurrent stream of heated air is also passed over the top of the trays to remove moisture which is released from

the material. The air is then exhausted through hoods to a scrubber and dust collector.


At the discharge end of the dryer, hot dry crystals drop through a vibrating chute to a surge hopper. The hopper serves as an emergency holding vessel for approximately $\frac{1}{2}$ -hr production in the event of temporary shut-down of downstream equipment. An electromagnetically vibrated screen spreader feeder receives the discharge from the surge hopper and delivers a uniform bed of product across the top of the ammonium perchlorate screen. Double-deck, electronically vibrated screens separate oversize and undersize crystals from the product. Fines and oversize particles are rejected through a chute to a dissolving tank.

Dry product from the screen is conveyed to the charging hole of one of two blenders. Each blender has a holding capacity of 20,000 lb. When one blender is filled to 50 per cent capacity, the product stream is diverted to the second unit, the charging door is closed, and the blender is rotated at a speed of 10 rpm for 15 to 30 min to provide a uniform mass of crystals.

On completion of the blending operation, the blender discharge spout is aligned with the automatic weighing scale. When the hopper is filled with 250 lb of product, the flow automatically stops and the contents are manually loaded into a plastic-lined drum. Silica gel is placed within the drum and the plastic liner sealed. The drums are covered and transported to the storage buildings.

For use as a propellant oxidizer, the product must meet exacting specifications, as listed in Table 6.4. This requires close production control over a large number of variables. In addition, the product is sampled at several points in the crystallizer operation, as well as at completion, to insure that the process is in proper control.

Safety. Since ammonium perchlorate is a Class II explosive, as defined by the U. S. Ordnance Safety Bulletin No. 159, a detailed safety program

 TABLE 6.4. SPECIFICATIONS FOR PROPELLANT AMMONIUM PERCHLORATE

Component	Minimum (%)	Maximum (%)
Water insoluble	—	0.10
Sulfated ash	—	0.25
Chlorates (NaClO_3)	—	0.15
Chlorides (NH_4Cl)	—	0.20
Sulfates [$(\text{NH}_4)_2\text{SO}_4$]	—	0.20
Bromates (NaBrO_3)	—	0.04
Nonalkali metals	—	0.04
Moisture	—	0.02
Reaction to methyl orange	Neutral	—
Ammonium perchlorate	99.0	—

is followed in its manufacture and handling. The plant is arranged in accordance with the Standard Quantity Distances specified for this classification. Reaction and wet processing are accomplished in one building and the drying and packaging operations are carried out in two identical, three-story buildings, situated the proper safe distance from all other operations. The flash drying, tunnel drying, and packaging operations are performed in individual fireproof units with explosion release walls. Each drying and packaging building is provided with a complete fire protection system. This includes hose racks at each floor, soda acid and carbon dioxide fire extinguishers, and automatic deluge systems, for the dryers, blenders, and complete buildings.

A more complete discussion of ammonium perchlorate safety requirements is given in Chapter 11.

Construction Materials. Prior to construction of the full scale plant, a study was made to determine the corrosion rate of various materials in ammonium perchlorate-sodium chloride solutions. On the basis of total immersion tests, as well as experience gained in a pilot plant operation, the suitable construction materials were selected. All welded piping and medium size vessels are Type 347 stainless steel. For the larger pieces of equipment, a compromise of Type 316 stainless steel proved desirable. The sections of the plant which are in contact with excess hydrochloric acid, such as the reactor system, are constructed of glass-lined steel or "Hastelloy C."

The original design included copper heat-transfer coils in the dryers. However, ammonium perchlorate dust created dust corrosion products which reduced the decomposition temperature of the perchlorate and resulted in a number of small fires. Consequently, the copper coils have been replaced with stainless steel coils.

New Developments. The increased demand for ammonium perchlorate by the missile industry has stimulated interest in developing new approaches toward its commercial manufacture. One method substitutes carbon dioxide²² for hydrochloric acid in the method just described, or:



A notable advantage of this process is the elimination of hydrochloric acid, which would undoubtedly be placed on the critical materials list during a wartime emergency. However, an economic evaluation of this method for full scale production has not been published.

Another method which has commercial potentialities involves the direct neutralization reaction between ammonia and perchloric acid, provided the perchloric acid can be obtained at a sufficiently low cost for the process to compete with that previously described. For example; the

perchloric acid could be formed in an electrolytic diaphragm-compartment cell⁴⁸ according to the reaction:



Sodium hydroxide could be a valuable by-product which might carry much of the cost of such an operation.

Long range experimental work for ammonium perchlorate manufacture would include an investigation of the potentialities of ion exchange processes, while it is conceivable that a number of other possibilities may exist.

Miscellaneous Perchlorates

Most other perchlorates can be made on a commercial scale from sodium perchlorate by double decomposition reactions with salts of the desired metals. Such processes are very similar in principle to those already described for potassium perchlorate and ammonium perchlorate. For example, lithium perchlorate may be manufactured in a corresponding manner by mixing concentrated solutions of lithium chloride and sodium perchlorate at an elevated temperature to crystallize out a crop of sodium chloride, while lithium perchlorate trihydrate separates on cooling.

In addition, any of the general methods listed on p. 73 may be used. For example, lithium perchlorate may be readily made by electrolysis of the chlorate⁴⁷ using 0.2 amp/sq cm at a temperature above 20°C, or by the reaction of perchloric acid on lithium hydroxide or carbonate.¹⁰ Another method is to react perchloric acid on lithium chloride, with heating to drive off the HCl.⁵⁵ Incidentally, this same method may be used on the chloride of almost any other metal, while a similar method, using the nitrate of the desired metal, has also been used.⁸³

Most of the more common inorganic perchlorates were prepared earlier by Serullas.⁷⁰ In most cases he used perchloric acid on the oxide or hydroxide of the metal, as in the case of the alkaline earths, lead, aluminum, copper, mercury and silver perchlorates. In the preparation of zinc, manganese and ferrous perchlorates, he reacted barium perchlorate with the sulfate of the metal concerned.

In some cases, a metal perchlorate may be prepared by the direct action of perchloric acid on the metal, as in the case of magnesium or zinc. However, such a reaction should not be attempted in the case of bismuth. Fichter and Jenny¹⁹ found that, upon heating such a mixture, a violent explosion resulted. This was further investigated by Nicholson and Reedy⁴⁹ who found that with bismuth, but with no other metal, an explosion invariably occurs upon heating with strong perchloric acid.

Ammonium perchlorate may also be used as the starting material for making other perchlorates on a laboratory scale, or even on a commercial

scale if the economics permit. For example, magnesium carbonate may be reacted with ammonium perchlorate, while the ammonia and carbon dioxide are driven off by heating.⁷³ In order to obtain anhydrous magnesium perchlorate, vacuum drying at a temperature of 250°C may be used.

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7. ANALYTICAL CHEMISTRY OF PERCHLORATES

The analytical chemistry of perchlorates is divided in two parts: the analysis of the perchlorates themselves and the use of perchlorates in analytical chemistry. This chapter will be concerned with the most important aspects of both of these phases of perchlorate chemistry.

ANALYSIS OF PERCHLORATES

Analyses of perchlorates are usually made by conversion of the perchlorate to chloride. The chloride is then determined by the usual volumetric or gravimetric method. Analyses are also made by reduction with titanous salts or precipitation as difficultly soluble salts, such as potassium perchlorate, tetraphenylarsonium perchlorate and quaternary ammonium complexes. In the special case of pure perchloric acid, analysis is made by titration of acidity.

All perchlorate methods suffer from interferences from a variety of materials. In general, when interferences are absent, most methods have been reported to yield satisfactory results. When interferences are present, however, corrections must be determined and applied or tedious separations must be made causing the result to be dependent upon the inherent inaccuracies of all the steps taken.

Qualitative Analysis

Qualitative analysis of perchlorates may be made by precipitation of difficultly soluble salts or by decomposition of perchlorate followed by analysis of decomposition products. The method of choice is dependent upon the amount of perchlorate, inherent interferences of the method and convenience.

Methylene blue, when free of zinc salts, reacts with perchlorate to yield a violet crystalline precipitate.^{5, 148} Persulfates and certain heavy metals interfere but the analysis may be made in the presence of chlorates. The method is reported to be extremely sensitive.

Potassium (also rubidium and cesium) salts precipitate perchlorate from cold saturated water solution. Ethanol-water solutions or anhydrous ethanol greatly reduce the solubility of the potassium perchlorate salt and are therefore preferred to cold water solutions.¹⁵⁵ Ammonium salts interfere. Methanol is not a satisfactory substitute for ethanol.⁹

Fusion of perchlorates with sodium carbonate converts perchlorates to chloride⁵ which can then be precipitated with silver nitrate. Chlorates and chlorides interfere but can often be satisfactorily removed.

Alkali perchlorates react with fused cadmium chloride to yield chlorine gas which forms a blue color with thio-Michler's ketone or a red color with fluorescein-bromide mixture. Feigl and Goldstein⁴¹ reported that 1 to 5 μg of perchlorate could be detected by this technique. Chlorates and nitrates interfered but were removed by fuming with concentrated hydrochloric acid. A similar method based on fusion with zinc chloride was described by Gooch and Kreider⁵¹ in which 50 μg could be detected.

Rubidium perchlorate crystals, formed on a microscope slide by the addition of rubidium chloride, are colored by the addition of potassium permanganate solution.¹⁰⁴ Microscopic examination of the dried crystals will detect as little as 0.1 per cent potassium perchlorate.

Strychnine sulfate crystals react slowly with perchlorate and become covered with hair-like crystals.⁵ This reaction was reported to be specific for dilute perchlorate solutions.

Tetraphenylarsonium chloride reacts with perchlorate to form an insoluble complex.¹⁷² Perrhenate, permanganate, iodate, mercuric chloride, stannic chloride and zinc chloride also form insoluble complexes and will interfere.

Copper-pyridine (Zwikk's reagent; 4 cc 10% CuSO_4 , 1 cc pyridine and 5 cc water) reacts with perchlorate to form characteristic crystals.¹⁶³ Persulfates, thiosulfates, chromates, permanganates and other anions interfere.

Quantitative Analysis

Quantitative analysis of perchlorates may be made by decomposition to chloride followed by analysis of chloride or by reducing agent consumed, precipitation as sparingly soluble salts, precipitation as sparingly soluble organic complexes and titration of liberated perchloric acid.

As discussed above, the methods are not specific for perchlorates and therefore the method of choice for a particular analysis is determined by the type of impurities present and the amount of the perchlorate in the material to be analyzed.

Decomposition Methods. Decomposition of perchlorate is usually the method of choice when perchlorate is the major component. Many reducing agents have been proposed. All include high heat. Chlorates, hypochlorite and chloride interfere but can be removed or can be determined and corrections applied.

Fusion with sodium carbonate in a platinum crucible decomposes perchlorate to chloride. The procedure is rapid and convenient and has been very useful for perchlorate analysis. Platinum from the crucible is a catalyst for the reaction. The chloride formed is determined by the Volhard method. This reaction is routinely used to analyze ammonium perchlorate.

A detailed procedure is given under the section "Analyses of Commercial Perchlorates." Modifications were studied by Dobroserdov and Erdmann⁸⁵ who described a detailed procedure to prevent loss of chloride during fusion. Biber and Barskaya¹³ modified the fusion by adding chromic sesquioxide (Cr_2O_3) in a carbon dioxide atmosphere and determined dichromate formed with sodium thiosulfate or the chloride by the Volhard method. Joan and Reedy⁶⁷ used potassium carbonate and manganous nitrate for the reduction to chloride. It was reported that manganous nitrate was converted to manganese dioxide which catalyzed the decomposition.

Ignition with ammonium chloride in a platinum crucible will decompose sodium and potassium perchlorate to chloride, according to Scott.¹¹⁹ Platinum from the crucible catalyzes the reaction. The chloride is determined by Volhard or by gravimetric silver chloride. A detailed procedure for the use of this method for the analysis of potassium perchlorate is given under the section "Analyses of Commercial Perchlorates."

Fusion with sodium peroxide in a Parr bomb was recommended by Crump and Johnson to convert perchlorate to chloride.⁸¹ It was reported that the method was rapid. Sodium peroxide fusion in an iron or nickel crucible has also been recommended for the decomposition of perchlorates.² It was reported that platinum catalyst was not necessary and the method was suitable for lithium perchlorate and other alkali perchlorates.

Sulfuric acid and starch were heated by Willard and Thompson¹⁷³ to reduce perchlorate to chlorine gas. Chlorine was then absorbed in alkaline arsenite and precipitated as silver chloride. Accurate results were reported but the concentration of sulfuric acid had to be carefully controlled.

Sulfuric acid and sulfur were heated to reduce perchlorate in biological substances by Durand.³⁷ Escaping vapors were trapped in sodium sulfite and chloride determined as silver chloride.

Fuming sulfuric acid and ferrous sulfate reduction by heat was recommended by Swift.¹⁵² Chlorine gas from the reduction was distilled and collected in alkaline sulfite solution. Chloride formed was determined by silver nitrate.

Sulfuric acid and potassium dichromate, potassium nitrate or potassium peroxydisulfate at 200°C have been used by Senften¹²² and Birkenbach and Goubeau¹⁵ to reduce perchlorate. Evolved gases were absorbed in saturated aqueous sulfur dioxide, sodium sulfite or sodium arsenite solutions. The resulting chloride was titrated with silver nitrate. Willard and Thompson¹⁷³ reported serious disadvantages in bumping and loss of perchloric acid when potassium dichromate was used.

Copper powder was used to reduce perchlorate by Scharer.¹¹⁶ The materials were heated in a covered crucible for 1 hr. Chloride was determined by silver nitrate.

Sodium oxalate was used to reduce perchlorate in nitrate ore by Groh and Neumeister.⁵⁴ Perchlorate was reduced by heating. Chloride so formed was determined by the Volhard method.

Manganese dioxide reduces perchlorate when heated at 600 to 700°C in a porcelain crucible, according to Lenher and Tosterud.⁸¹ Chloride was determined by Volhard. A blank was necessary.

Titanous salts reduce perchlorate to chloride when heated in an acid solution, and in an inert atmosphere. The method is not in general use due to the problems associated with the apparent need for inert atmosphere and the instability of the reagent. Vil'yamovich¹⁶⁰ reduced perchlorate with strong sulfuric-hydrochloric acid mixture and 400 per cent excess titanous sulfate, refluxing 2 hr. A carbon dioxide atmosphere was used and excess titanous ion was titrated with potassium permanganate. Peebles¹⁰⁵ reduced small quantities of perchlorate with titanous sulfate in sulfuric acid. A distillation apparatus was used and hydrochloric acid distilled into sodium hydroxide to avoid loss. Meldrum and his co-workers⁹⁵ completely reduced potassium perchlorate by refluxing for 5 min after addition of 100 per cent excess titanous chloride. It was reported that at least 33 per cent sulfuric acid must be maintained. Huskens and Gaty⁶⁵ reduced potassium perchlorate in an inert atmosphere with standard titanous chloride in hot 6*N* hydrochloric acid. Excess titanous chloride was back titrated with standard ferrous sulfate. Schnell¹¹⁸ reduced perchlorate with trivalent titanium in sulfuric acid under reflux. Aluminum was added to reduce tetravalent titanium as formed. Chloride formed was titrated with silver nitrate. Eagles³⁸ reduced potassium perchlorate with standard titanous chloride by boiling 3 min in carbon dioxide atmosphere. Back titration of excess titanous ion was with standard ceric ammonium sulfate.

Electrolytic reduction of perchlorate to chloride in sulfuric acid was described by Heller.⁵⁷ It was reported that the electrolysis required considerable time and titanous salts were not necessary.

Combustion of perchlorate in a calorimeter bomb to reduce the perchlorate in explosives was recommended by Meldrum and his co-workers.⁹⁵ Chloride so formed was determined by the Volhard method. The method was reported to be more accurate and faster than the titanous method.

Precipitation of Insoluble Salts. Perchlorates form no insoluble salts with heavy metals or alkaline earth metals. Only potassium, rubidium and cesium perchlorates are sparingly soluble and these have been used for quantitative estimation. The method is useful for perchlorate analysis but suffers from the problems associated with treatment to remove interfering materials or minimize solubility.

Arndt and Nachtwey³ reacted the perchlorate in a series of organic compounds with alcoholic potassium acetate. The precipitated potassium perchlorate was weighed and perchlorate estimated.

Chaney and Mann²⁵ studied potassium acetate in absolute alcohol as a precipitant for inorganic perchlorates. The solutions were heated to near boiling, allowed to stand 2 to 3 hr, filtered, washed, dried and weighed. Perchlorates of aluminum, barium, cadmium, copper, cobalt, nickel, lead and zinc were determined.

Smeets¹²⁷ also dissolved perchlorates in absolute ethanol, added cold saturated ethanolic potassium acetate, filtered potassium perchlorate, washed in absolute ethanol and weighed. It was reported that the method was suitable for lithium, sodium, nickel, cobalt, zinc, lead, aluminum, chromium and iron perchlorates. For silver, magnesium, manganese, calcium, barium, strontium and ammonium perchlorates, preliminary treatment with sodium carbonate was recommended. Bircumshaw and Newman¹⁶ reported that the method of Smeets¹²⁷ was low for perchlorate from ammonium perchlorate. Low values were attributed to incomplete extraction of sodium perchlorate when treated with sodium carbonate.

Precipitation of Organic Complexes. Perchlorates form insoluble complexes with quaternary ammonium compounds and organo-arsonium compounds. These have been used for quantitative estimation of large quantities of perchlorates as well as of trace quantities. There are many interferences.

Nitron precipitation was studied by Marvel and du Vigneaud⁹⁰ who report 0.0082 g/100 ml water for the solubility of nitron perchlorate. It was reported that many ions interfere and the reagents are not particularly stable. Leimbach⁸⁰ treated Chili saltpeter with concentrated hydrochloric acid to eliminate the interference of nitrates and chlorates with nitron perchlorate precipitation. Loebich⁸⁴ used more concentrated reagent to eliminate interference of chloracetic acid from nitron perchlorate. Vürtheim¹⁶² treated Chili saltpeter with Devarda's alloy to reduce nitrate and chlorate. Perchlorate was not affected and was precipitated as nitron perchlorate. It was reported that results agreed with the ignition method and seemed more reliable. Willard and Kassner¹⁷⁰ treated lead perchlorate with sulfate to remove lead and precipitated perchlorate as nitron perchlorate. It was reported that excellent results were obtained with twice the theoretical nitron but perchlorate results were not as good as the lead results. Rohrback and Cady¹¹³ reacted fluorine perchlorate with sodium hydroxide solution and precipitated perchlorate as nitron perchlorate according to the method of Loebich.⁸⁴

Methylene blue precipitation of perchlorates was described by Bers and Feldmeyer¹¹ who proposed a method by which methylene blue perchlorate could be washed free of nitrate interference and determined gravimetrically or colorimetrically. Krüger and Tschirch⁷⁹ described a method based on methylene blue perchlorate in which as little as 0.01 to 0.003

mg perchlorate in aqueous solution could be detected. Bolliger¹⁹ dissolved potassium perchlorate in water and treated the solution with a measured volume of methylene blue chloride. The precipitate was filtered and the excess methylene blue chloride titrated with picric acid. It was reported that as little as 1 mg perchlorate could be determined. Junck and Küpper⁶⁸ described a colorimetric method in which zinc sulfate was used to inhibit precipitation and increase the color sensitivity. It was reported that potassium perchlorate in the range of 0 to 1 per cent could be estimated to 0.01 per cent in about 1 hr. In a similar manner Federova⁴⁰ applied Hahn's reagent⁵⁵ to determine perchlorate colorimetrically. 0.0012 per cent perchlorate in 0.9 per cent chlorate was detected.

Tetraphenyl arsonium chloride precipitation of perchlorates was studied by Willard and Smith.¹⁷² It was reported that the precipitate could be weighed or the excess tetraphenylarsonium chloride could be titrated iodometrically. Many interferences were reported, such as, perrhenate, permanganate, iodate, mercuric chloride, stannous chloride and zinc chloride. Tetraphenylarsonium chloride was reported superior to nitron as a precipitant.

Copper-pyridine complex precipitation of perchlorates was studied by Bodenheimer and Weiler.¹⁸ Cupric nitrate-pyridine solution was saturated with sodium chloride and reacted with perchlorate for a few hours. The precipitate was filtered and the excess reagent read on a colorimeter. Perchlorate was estimated from standards.

Titration of Perchloric Acid. Perchloric acid is a strong acid and is readily titrated with standard base. Foreign mineral acids, of course, interfere and proper corrections must be applied. Electrolysis of heavy metal perchlorates deposits heavy metals and liberates perchloric acid. Perchloric acid so liberated can be titrated with standard base.

Titration of pure perchloric acid solution has been described by Wichers and his co-workers.¹⁶⁵ Perchloric acid was diluted with water and titrated with sodium hydroxide.

Electrolysis of heavy metal perchlorates has been described by Goldblum.⁵⁰ Cobalt and nickel perchlorates were electrolyzed to deposit metals and the remaining perchloric acid titrated with standard base. Willard and Kassner¹⁷⁰ electrolyzed lead perchlorate to determine lead and titrated resulting perchloric acid with standard base. Lindstrand⁸³ deposited iron electrolytically from iron perchlorate and determined perchloric acid by titration.

Analyses of Commercial Perchlorates

Perchloric Acid. Perchloric acid is normally analyzed by the titration of acidity. The usual impurities—silica, chloride, nitrogen compounds,

sulfate, heavy metals and iron—are determined by established procedures for these materials without interference from the perchlorate anion. The American Chemical Society Committee on Analytical Reagents¹ outlines the following procedure for assay of this material:

“Weigh about 3 ml, dilute to 60 ml and titrate with 1*N* sodium hydroxide using phenolphthalein indicator. One ml of 1*N* sodium hydroxide corresponds to 0.1005 g HClO_4 .”

Ammonium Perchlorate. Ammonium perchlorate is analyzed by reducing the perchlorate to chloride by fusion in a platinum crucible with sodium carbonate.² The chloride thus formed is determined by titration with standard silver nitrate. Chlorides, chlorates, bromates and alkali perchlorates interfere and corrections must be applied. A typical analysis of technical grade material is presented in Table 7.1. A consumer of this material¹⁵⁸ has specified the following method of analysis:

Sample Preparation. From each composite sample, prepare a composite solution (solution “A”) as follows: Dissolve 50.0 g of the sample in about 300 ml of hot distilled water. Cool the solution to room temperature, transfer to a 500-ml volumetric flask, and dilute to volume.

1 ml solution “A” = 0.100 g sample

Moisture.

Reagents: Methanol, anhydrous.

Standard KF (Karl Fischer) reagent, H_2O equiv. approx. 3 mg/ml.

Standard water-methanol solution, approx. 3 mg H_2O /ml.

Sodium tartrate dihydrate, Merck reagent grade preferred.

Apparatus: An aquameter. (Beckman “Aquameter” Model KF-2 has been found suitable.)

Preparation of KF Reagent. Dissolve 169.4 g of resublimed iodine in 538 ml of pyridine (reagent grade, water content less than 0.1 per cent), and add 1334 ml of anhydrous methanol (reagent grade). Cool the solution to about 5°C in an ice bath, and add 90 ml of liquid sulfur dioxide in increments of 15 to 20 ml, with stirring between additions. Allow the reagent to stand at least 1 week to stabilize, so that daily standardizations are subsequently sufficient.

Standardization of Reagents. To determine the strength of the KF reagent in terms

TABLE 7.1. TYPICAL ANALYSIS OF TECHNICAL AMMONIUM PERCHLORATE²

Ammonium perchlorate (NH_4ClO_4)	99.9%
Chloride (Cl)	0.020
Chlorate (ClO_3)	0.004
Bromate (BrO_3)	0.002
Sulfate (SO_4)	trace
Nonalkali metals	0.002
Moisture	0.004
Water insoluble	0.003
Ash	0.05
Reaction—methyl orange	neutral

of equivalent volume of water-methanol solution, put about 60 ml of anhydrous methanol into the titration beaker of the Aquameter, add a slight excess of KF reagent, and back-titrate with water-methanol solution. Run in 5 to 8 ml. of KF reagent, and again back-titrate with water-methanol solution. Repeat twice the addition and back-titration, to provide triplicate determination of the equivalence ratio, and calculate the ratio (r) of water-methanol solution of KF reagent. The range of the ratios calculated from the three titrations should be not greater than 0.04.

To determine the water content of the water-methanol solution, neutralize the water in a 60-ml portion of anhydrous methanol as for the determination of solution equivalence, then add to the titration solution an accurately weighed portion of 0.15 to 0.20 g of sodium tartrate dihydrate reagent by dropping a 1-ml beaker containing the reagent into the solution. Run in a slight excess of KF reagent, and back-titrate with water-methanol solution. Duplicate standardizations should agree within 0.065 mg H₂O/ml of reagent.

Calculation:

$$\text{mg H}_2\text{O per ml H}_2\text{O-MeOH solution} = \frac{1000 \times 0.1566W}{rR - S} = E$$

where W = weight of sodium tartrate dihydrate in grams

r = ml of H₂O-MeOH solution/ml KF reagent

R = ml of KF reagent used

S = ml of H₂O-MeOH solution used for back-titration.

The water-methanol solution should be standardized weekly, and the KF reagent must be standardized daily.

"Determination of Water. Neutralize the water in a 60-ml portion of anhydrous methanol (as in the standardization of the reagents), and introduce a sample of 20 to 50 g of perchlorate from a stoppered weighing bottle. Determine the weight of the sample from the weight of the bottle with and without the sample. Run in a visible excess of KF reagent, and back-titrate with water-methanol solution.

Calculation:

$$\% \text{ H}_2\text{O} = \frac{(rR - S)E \times 100}{1000W}$$

where r = ml of H₂O-MeOH solution/ml KF reagent

R = ml of KF reagent used

S = ml of H₂O-MeOH solution used for back-titration

E = mg H₂O/ml H₂O-MeOH solution

W = weight of sample in grams.

"Water Insoluble. Dissolve 25.0 g of the composite sample in about 250 ml of distilled water, and filter the solution through a tared Selas crucible of medium porosity. Wash with distilled water, dry for 1½ hr at 105°C, cool, and weigh.

Calculation:

$$\% \text{ water insoluble} = \frac{\text{weight of residue}}{\text{weight of sample}} \times 100$$

"pH of Water Solution. Add 50 ml of freshly boiled distilled water to 20 g of com-

posite sample. Stir the solution well, and cool to room temperature. Measure the pH to the nearest 0.01 unit with any standard electrometric equipment.

"Chloride."

Reagents: Nitric acid, concentrated.

Silver nitrate solution (approx. 0.10*N*).

Standard chloride solution, 0.022 g NaCl or 0.028 g KCl/l., equivalent to 0.020 g NH₄Cl/l.

Pipette 10 ml of solution "A" into a 100-ml volumetric flask, dilute to volume with distilled water, and mix thoroughly. Pipette 10 ml of this diluted aliquot into a Nessler tube, and dilute to 30 ml with distilled water. Add 30 ml of distilled water to each of three other Nessler tubes. Add 1 ml concentrated HNO₃ and 1 ml of 0.1*N* AgNO₃ solution to sample and blanks. To one of the blanks, add sufficient standard chloride solution to match approximately the turbidity of the sample; then to one of the other blank solutions, add 1.0 ml more of standard chloride solution, and to the other add 1.0 ml less standard chloride than was added to the first blank. Allow the solutions to stand 15 min, then visually compare the sample with the standards. Select the standard that most nearly matches the sample. If more than 4.0 ml of standard chloride solution is used to match the sample, use 5 ml of diluted aliquot and repeat the procedure.

Calculation:

$$\% \text{ chloride as NH}_4\text{Cl} = \frac{0.000020V \times 100}{0.01S} = \frac{0.20V}{S}$$

where V = volume of standard chloride solution required to match or exceed the turbidity of the sample and S = volume of diluted aliquot used.

"Sulfated Ash." (weighed as Na₂SO₄, calculated as NaClO₄).

Reagent: Sulfuric acid, approx. 50%.

Grind at least 5 g of dried sample to a fine powder. Add about 0.2 g of sample to a previously ignited and tared silica crucible. Cover, and heat carefully with a Bunsen flame until the portion has decomposed. Continue the ignition of small increments until the entire sample has been decomposed and the volatile salts have been driven off. Allow the crucible to cool, and add a few drops of 50% H₂SO₄. Heat again, and complete the volatilization of H₂SO₄ at a dull red heat. Cool in a desiccator, and weigh.

Calculation:

$$\% \text{ sulfated ash as NaClO}_4 = \frac{\text{wt. of residue} \times 122.5 \times 100}{\text{wt. of sample} \times 71} = \frac{\text{wt. of residue}}{\text{wt. of sample}} \times 172$$

"Bromate."

Reagents: Potassium iodide, anal. reagent.

Hydrochloric acid, dilute, 1:9.

Starch indicator solution, 0.2%.

Standard Na₂S₂O₃ solution, 0.02*N*.

Transfer 100 ml of solution "A" to a 500-ml glass-stoppered Erlenmeyer flask, and add 100 ml of freshly boiled and cooled distilled water. Add 0.5 g of potassium iodide, 5 ml of 1:9 HCl, and 5 ml of starch indicator solution. Mix well and allow to stand in a dark place for 1 hour. Titrate with standard sodium thiosulfate solution until the blue color disappears. Run a blank on the reagents.

Calculation:

$$\% \text{ bromate as } \text{NH}_4\text{BrO}_3 = \frac{0.0243N(V - v) \times 100}{0.1S} = \frac{24.3N(V - v)}{S}$$

where V = ml sodium thiosulfate required by sample

v = ml sodium thiosulfate required by blank

N = normality of sodium thiosulfate solution

S = volume of solution "A" used.

"Chlorate.

Reagents: Hydrochloric acid, dilute, 1:1.

Standard chlorate solution, 0.06 g KClO_3/l .

o-Tolidine reagent, 1 g/l. in 10% HCl .

Transfer two aliquots (normally 10 and 20 ml) of solution "A" to 125-ml glass-stoppered Erlenmeyer flask, and in a series of four similar flasks place portions of standard chlorate solution ranging from 1.0 to 4.0 ml in steps of 1.0 ml. Dilute the contents of each flask to approximately 40 ml with distilled water, and add 40 ml of 1:1 HCl to each. Warm the flasks to 40°C , and hold for 30 min. Add 1 ml of *o*-tolidine reagent to each, and let stand for 5 min. Compare the colors of sample and standards in Nessler tubes.

If the color of the sample solution does not fall within the range of the standards, repeat the procedure with a larger or smaller aliquot and a new set of standards.

Calculation:

$$\% \text{ chlorate as } \text{NH}_4\text{ClO}_3 = \frac{0.00005V \times 100}{0.1S} - 0.69B = \frac{0.05V}{S} - 0.69B$$

where S = volume of aliquot of solution "A"

V = volume of standard chlorate solution required to match or exceed the color developed by the sample

B = % bromate as NH_4BrO_3 .

"Perchlorate.

Reagents: Sodium carbonate, anhydrous, anal. reagent grade.

Nitric acid, concentrated.

Sodium bicarbonate, reagent, ACS specification.

Potassium chromate, 5% solution.

Standard silver nitrate solution, 0.1*N*.

Weigh accurately about 0.5 g of finely ground dry sample into a platinum crucible, and mix carefully with 4.0 g of anhydrous Na_2CO_3 . Overlay the mixture with 1.0 g of Na_2CO_3 . Cover the crucible, and slowly raise the temperature with a Bunsen burner until the contents are completely fused, and hold the temperature just above the fusion point for 10 min. Allow the crucible to cool. Transfer the melt quantitatively to a 250-ml wide-mouth Erlenmeyer flask with a minimum quantity of distilled water. Cover with a watch glass, and make the solution slightly acid by adding concentrated HNO_3 slowly from a dropping bottle, using litmus paper as an indicator. When all the melt is in solution and the solution is barely acid, add solid sodium bicarbonate in small portions until the solution is barely alkaline. At this point the volume should not exceed about 75 ml. Add 0.5 ml of potassium chromate indicator, and titrate with standard 0.1*N* AgNO_3 solution. Prepare and titrate a blank containing the quantities of Na_2CO_3 , HNO_3 , and NaHCO_3 in the same volume of solution as the sample.

Calculation:

$$\% \text{ perchlorate as } \text{NH}_4\text{ClO}_4 = \frac{0.1175N(A - B) \times 100}{W} - (2.20C + 1.16D + 0.96E)$$

where A = ml AgNO_3 required to titrate sample

B = ml AgNO_3 required to titrate blank

N = normality of AgNO_3 solution

C = per cent NH_4Cl in sample

D = per cent NH_4ClO_3 in sample

E = per cent NaClO_4 in sample

W = weight of sample."

Potassium Perchlorate. Potassium perchlorate is analyzed by reducing the perchlorate to chloride by heating with ammonium chloride in a platinum crucible.² The chloride thus formed is determined by titration with standard silver nitrate. Chlorides and chlorates interfere and corrections must be applied. A typical analysis of technical grade material is presented on Table 7.2. A consumer of this material¹⁵⁷ has specified the following method of analysis:

"Sample Preparation. From each composite sample prepare a composite solution (solution "A") as follows: Dissolve 50.0 g of the sample in about 300 ml of hot distilled water. Cool the solution to room temperature, transfer to a 500-ml volumetric flask, and dilute to volume.

1 ml solution "A" = 0.100 g sample

"Moisture.

Reagents: Methanol, anhydrous.

Standard water-methanol solution, approx. 3 mg H_2O /ml.

Standard KF (Karl Fischer) reagent, H_2O equiv. approx. 3 mg/ml.

Sodium tartrate dihydrate, Merck reagent grade preferred.

Apparatus: An aquameter. (Beckman Model KF-2 has been found suitable)

"Preparation of KF Reagent. Dissolve 169.4 g of resublimed iodine in 538 ml of pyridine (reagent grade, water content less than 0.1%), and add 1334 ml of anhydrous methanol (reagent grade). Cool the solution to about 5°C in an ice bath, and add 90 ml of liquid sulfur dioxide in increments of 15 to 20 ml, with stirring between additions.

TABLE 7.2. TYPICAL ANALYSIS OF TECHNICAL POTASSIUM PERCHLORATE²

Potassium perchlorate (KClO_4)	99.8%
Chloride (Cl)	0.085
Chlorate (ClO_3)	trace
Bromate (BrO_3)	0.002
Hypochlorite (ClO)	none
Sodium (Na)	0.066
Calcium and magnesium (Ca & Mg)	none
Moisture	0.016
Water insoluble	0.003
Color	white

Allow the reagent to stand at least 1 week to stabilize, so that daily standardizations are subsequently sufficient.

Standardization of Reagents. To determine the strength of the KF reagent in terms of equivalent volume of water-methanol solution: Put about 60 ml of anhydrous methanol into the titration beaker of the Aquameter, add a slight excess of KF reagent, and back-titrate with water-methanol solution. Run in 5 to 8 ml of KF reagent, and again back-titrate with water-methanol solution. Repeat twice the addition and back-titration, to provide triplicate determination of the equivalence ratio, and calculate the ratio (r) of water-methanol solution to KF reagent. The range of the ratios calculated from the three titrations should be not greater than 0.04.

To determine the water content of the water-methanol solution: Neutralize the water in a 60-ml portion of anhydrous methanol as for the determination of solution equivalence, then add to the titration solution an accurately weighed portion of 0.15 to 0.20 g of sodium tartrate dihydrate reagent by dropping a 1-ml beaker containing the reagent into the solution. Run in a slight excess of KF reagent, and back-titrate with water-methanol solution. Duplicate standardizations should agree within 0.065 mg H_2O /ml of reagent.

Calculation:

$$\text{mg H}_2\text{O per ml H}_2\text{O-MeOH solution} = \frac{1000 \times 0.1566W}{rR - S} = E$$

where W = weight of sodium tartrate dihydrate in grams

r = ml of $\text{H}_2\text{O-MeOH}$ solution/ml KF reagent

R = ml of KF reagent used

S = ml of $\text{H}_2\text{O-MeOH}$ solution used for back-titration

The water-methanol solution should be standardized weekly, and the KF reagent must be standardized daily.

Determination of Water. Neutralize the water in a 60-ml portion of anhydrous methanol (as in the standardization of the reagents), and introduce a sample of 20 to 50 g of perchlorate from a stoppered weighing bottle. Determine the weight of the sample from the weight of the bottle with and without the sample. Run in a visible excess of KF reagent, and back-titrate with water-methanol solution.

Calculation:

$$\% \text{ H}_2\text{O} = \frac{(rR - S)E \times 100}{1000W}$$

where r = ml of $\text{H}_2\text{O-MeOH}$ solution/ml KF reagent

R = ml of KF reagent used

S = ml of $\text{H}_2\text{O-MeOH}$ solution used for back-titration

E = mg H_2O /ml $\text{H}_2\text{O-MeOH}$ solution

W = weight of sample in grams

Water Insoluble. Dissolve 25.0 g of the composite sample in about 250 ml of distilled water, and filter the solution through a tared Selas crucible of medium porosity. Wash with distilled water, dry for $1\frac{1}{2}$ hr at 105°C , cool, and weigh.

Calculation:

$$\% \text{ water insoluble} = \frac{\text{weight of residue}}{\text{weight of sample}} \times 100$$

"pH of Water Solution. Add 50 ml of freshly boiled distilled water to 20 g of composite sample. Stir the solution well, and cool to room temperature. Measure the pH to the nearest 0.01 unit with any standard electrometric equipment.

"Chloride.

Reagents: Nitric acid, concentrated.

Silver nitrate solution (approx. 0.10*N*)

Standard Chloride solution, 0.016 g NaCl or 0.028 g KCl/l.

Pipette 10 ml of solution "A" into a 100-ml volumetric flask, dilute to volume with distilled water, and mix thoroughly. Pipette 10 ml of this diluted aliquot into a Nessler tube, and dilute to 30 ml with distilled water. Add 30 ml of distilled water to each of three other Nessler tubes. Add 1 ml concentrated HNO₃ and 1 ml of 0.1*N* AgNO₃ solution to sample and blanks. To one of the blanks, add sufficient standard chloride solution to match approximately the turbidity of the sample; then to one of the other blank solutions, add 0.2 ml more of standard chloride solution, and to the other add 0.2 ml less standard chloride than was added to the first blank. Allow the solutions to stand 15 min, then visually compare the sample with standards. Select the standard that most nearly matches the sample. If more than 2.5 ml of standard chloride solution is used to match the sample, use 5 ml of diluted aliquot and repeat the procedure.

Calculation:

$$\% \text{ chloride as KCl} = \frac{0.28V}{S}$$

where *V* = volume of standard chloride solution required to match or exceed the turbidity of the sample and *S* = volume of diluted aliquot used.

"Bromate.

Reagents: Potassium iodide, anal. reagent.

Hydrochloric acid, dilute, 1:9.

Starch indicator solution, 0.2%.

Standard Na₂S₂O₃ solution, 0.02*N*.

Transfer 100 ml of solution "A" to a 500-ml glass-stoppered Erlenmeyer flask, and add 100 ml of freshly boiled and cooled distilled water. Add 0.5 g of potassium iodide, 5 ml of 1:9 HCl, and 5 ml of starch indicator solution. Mix well and allow to stand in a dark place for 1 hour. Titrate with standard sodium thiosulfate solution until the blue color disappears. Run a blank on the reagents.

Calculation:

$$\% \text{ bromate as KBrO}_3 = \frac{27.83N(V - v)}{S}$$

where *V* = ml sodium thiosulfate required by sample

v = ml sodium thiosulfate required by blank

N = normality of sodium thiosulfate solution

S = volume of solution "A" used.

"Chlorate.

Reagents: Hydrochloric acid, dilute, 1:1.

Standard chlorate solution, 0.06 g KClO₃/l.

o-Tolidine reagent, 1 g/l. in 10% HCl.

Transfer an aliquot (normally 5 ml) of solution "A" to a 125-ml glass-stoppered Erlen-

meyer flask, and in a series of four similar flasks place portions of standard chlorate solution ranging from 3.0 to 6.0 ml in steps of 1.0 ml. Dilute the contents of each flask to approximately 40 ml with distilled water, and add 40 ml of 1:1 HCl to each. Warm the flasks to 40°C, and hold for 30 min. Add 1 ml of *o*-tolidine reagent to each, and let stand for 5 min. Compare the colors of sample and standards in Nessler tubes. If the color of the sample solution does not fall within the range of the standards, repeat the procedure with a larger or smaller aliquot and a new set of standards.

Calculation:

$$\% \text{ chlorate as KClO}_3 = \frac{0.06V}{S} - 0.73B$$

where S = volume of aliquot of solution "A"

V = volume of standard chlorate solution required to match or exceed the color developed by the sample

B = % bromate as KBrO_3 .

"Calcium and Magnesium."

Reagents: Hydrochloric acid, concentrated.

Dihydrogen ammonium phosphate solution, saturated.

Ammonium oxalate solution, 10%.

Ammonium hydroxide, concentrated.

Ca-Mg standard solution (1.78 g CaCO_3 + 2.09 g MgCO_3 dissolved in minimum excess of dilute HCl and diluted to 1000 ml).

Transfer 100 ml of solution "A" to a 250-ml beaker, and in a series of 4 similar beakers place portions of standard Ca-Mg solution ranging from 0.5 to 2.0 ml in steps of 0.5 ml (representing 0.010%, 0.020%, 0.030%, and 0.040%, respectively, of combined oxides), with 100 ml of distilled water. Add 2 ml of concentrated HCl, 5 ml of ammonium phosphate solution, 5 ml of ammonium oxalate solution and 10 ml of concentrated NH_4OH to each beaker. Let stand overnight, and compare the volume of precipitate from the test solution with that from the standards. Report the percentage corresponding to the standard showing equal or the next greater volume of precipitate.

"Perchlorate."

Reagents: Ammonium chloride, reagent grade (ground to 200 mesh).

Potassium chromate solution, 5%.

Standard silver nitrate solution, 0.1N.

Grind about 1 to 2 g of the composite sample in an agate mortar to an impalpable powder, and dry at least 4 hr at 105°C. Mix intimately an accurately weighed portion of about 0.5 g of the dried ground sample with 1.5 g of ground NH_4Cl in a platinum crucible. Cover the mixture with an additional 0.5 g of NH_4Cl , and cover the crucible. Prepare a blank of 2.0 g of ammonium chloride in another crucible, and carry the blank through the procedure in parallel with the sample. Place the crucibles in a cold muffle furnace. Raise the temperature of the furnace to 600°C in about 1½ hours. Remove the crucibles, add 2 g of NH_4Cl and complete the volatilization at 600°C. Transfer the cooled melt quantitatively to a 250-ml wide-mouth Erlenmeyer flask with a minimum of distilled water. The total volume should be approximately 75 ml. Add 0.5 ml of potassium chromate indicator, and titrate with 0.1N standard silver nitrate solution.

Calculation:

$$\% \text{ perchlorate as KClO}_4 = \frac{0.13855N(A - B) \times 100}{W} - (1.86C + 1.13D)$$

where A = ml AgNO_3 required to titrate sample
 B = ml AgNO_3 required to titrate blank
 N = normality of AgNO_3 solution
 C = % KCl in sample
 D = % KClO_3 in sample
(W = weight of sample in grams.)"

USES OF PERCHLORIC ACID AND PERCHLORATES IN ANALYTICAL CHEMISTRY

Perchloric acid and perchlorates have found extensive applications in the field of chemical analysis. One of the oldest uses of perchloric acid has been as a precipitant for potassium in the quantitative determination of this element. Perchloric acid (usually in conjunction with nitric and sulfuric acids), has also been of use as an agent for the destruction of organic matter (wet ashing). In inorganic analysis, it has been used as an agent and reaction-medium in the digestion, oxidation and separation of many mining, metallurgical and related products, and as a dehydrating agent in the determination of silica.

More recently, perchloric acid has been used very successfully in the field of nonaqueous titrimetry, especially in the determination of organic bases. It has also been applied as a deproteinization agent in biochemical work, where it was reported to be superior to trichloroacetic acid.

In oxidimetric analysis, perchloric acid, complexed to cerium (IV), has made possible or facilitated the determination of many hydroxylated organic compounds, whose evaluation by older methods was difficult or cumbersome.

Perchlorates (especially magnesium perchlorate) have found considerable uses as drying agents in the determination of carbon dioxide and in combustion analysis.

Many other uses of perchloric acid and its salts have been reported. Some examples of these are: mercurous perchlorate as a volumetric reagent for iron, and for the determination of chlorides and bromides; color reactions of perchloric acid with steroids; standardization of sodium thiosulfate, using perchloric acid; microidentification of cupric ion, etc.

Determination of Potassium with Perchloric Acid

In 1831, G. Serullas¹²⁴ published a sensitive test for the separation and detection of potassium by perchloric acid. This test was improved by future investigators, and developed into a quantitative method for the determination of potassium. It was based on the insolubility of potassium perchlorate in 97 per cent ethanol (or ethyl acetate), and the solubility of other perchlorates in these solvents. The method gave accurate results, and has largely superseded the more expensive chloroplatinate procedure.

Smith and co-workers^{144, 145} made a study of the conditions to be observed in the determination of potassium as potassium perchlorate in the presence of sodium and lithium and of the separation of potassium perchlorate as an intermediate in the determination of potassium by chloroplatinate. Bunge²⁰ determined potassium as perchlorate in explosives containing ammonium nitrate. Smith¹²⁹ and Willard and Smith¹⁷¹ also investigated the solubility of alkali and alkaline earth perchlorates in water and in various organic solvents, such as methyl-, ethyl-, and *n*-butyl alcohol, ethyl acetate, etc. Smith¹²⁸ made a study of the precipitation of potassium perchlorate from a warm water solution of sodium and potassium perchlorates by addition of large volumes of *n*-butyl alcohol. Smith¹²⁹ investigated the solubilities of alkali metal perchlorates in mixed organic solvents.

Details of the perchlorate method for the quantitative determination of potassium are given in most textbooks on analytical chemistry.^{120, 168} Morris⁹⁶ published a comprehensive review of the method.

Use of Perchloric Acid in the Destruction of Organic Matter (Wet Ashing)

The removal or destruction of organic matter prior to the determination of mineral constituents in organic materials may frequently be carried out by "wet-ashing" at elevated temperatures with nitric and perchloric acid mixtures. The use of nitric acid with perchloric acid aids in preoxidation of easily oxidizable organic matter and thus prevents the vigorous and often explosive reaction of hot perchloric acid alone on organic matter. Destruction of organic substances for the determination of nitrogen in the Kjeldahl digestion may also be carried out with perchloric acid either in absence or presence of selenic acid as catalyst.

Kahane,⁷³ Matutano,⁹² Burton and Prail,²¹ and Young and Campbell¹⁷⁵ discussed the hazards involved, the precautions necessary, and the best conditions to be used in wet-ashing with perchloric acid.

Smith¹³⁵ described the destruction of formic, oxalic, tartaric, and citric acids, formaldehyde, cyclic ring nitrogen compounds, and animal proteins by means of hot perchloric acid, together with and without nitric acid and vanadium as catalyst. The oxidation of sulfur was also discussed. Smith and Sullivan¹⁴⁷ gave detailed directions for the destruction of organic matter and oxidation of chromium in the analysis of chromium in chrome leather. Smith¹³⁷ described the use of a mixture of nitric, perchloric and sulfuric acids, containing potassium dichromate as catalyst, for the determination of copper in gas-mask carbon. The destruction of cellulose by wet-ashing by the use of mixed nitric-perchloric-sulfuric acids, and the trace-element determination of copper and mercury in pulp and paper were described by Smith.¹³⁶ Smith¹³³ also discussed in detail the use of nitric, perchloric, sul-

furic, and phosphoric acids, and their application to the analysis of organic and inorganic materials. Kahane⁷¹ likewise presented a good review of this field.

A wet-ashing technique for the determination of siliceous particles in the lungs was described by Kahane.⁷² Fabre and Kahane³⁹ made use of perchloric acid in the digestion of toxicological material for the determination of arsenic, mercury, copper, manganese and chromium.

Kagi⁶⁹ discussed the ashing of milk and milk products by perchloric-nitric acid mixture, and gave a table showing minimum quantities of acids for complete ashing. Methods which led to and prevented explosions were also given.

Hamlin⁵⁶ reported on the wet-ashing of organic matter and compared the oxidation of cotton with nitric acid or hydrogen peroxide with the use of mixtures of perchloric, nitric and sulfuric acids. Safe and rapid procedures for cotton and other textile fibers were given. Wet-ashing of biological material from plant or animal sources prior to the determination of mineral constituents was described by Giesekeing and co-workers⁴⁵ and by Gerritz.⁴⁴

Wolesensky¹⁷⁴ found wet-ashing by nitric and perchloric acids to be superior to sodium peroxide fusion (Parr method) in the determination of sulfur in rubber. Smith and Deem¹⁸⁸ used the perchloric acid method for determining sulfur in coal. Kahane and Kahane⁷⁵ applied a similar procedure to the determination of free or combined sulfur in rubber and various other organic and inorganic substances. Kahane also recommended wet-ashing methods for the determination of iodine in organic compounds,⁷⁶ and of arsenic in medicinals.⁷⁰

The use of perchloric acid in Kjeldahl digestions was exemplified by the work of various investigators, who were able to considerably shorten the digestion period by the introduction of this acid. Pepkowitz and co-workers¹⁰⁶ suggest the use of 35 per cent perchloric acid in conjunction with selenium oxychloride as catalyst. The average digestion time for 1 g samples was approximately 30 min. It was reported that no explosive hazards were involved.

Mallol⁸⁶ treated organic nitrate compounds with selenium (0.05 g) dissolved in 20 cc concentrated sulfuric acid and heated with agitation while adding concentrated perchloric acid dropwise to digest the organic matter. Digestion time was only 4 min. Addition of glucose⁸⁸ prevented low nitrogen recovery.

Marqués and Capont⁸⁹ successfully applied Mallol's method⁸⁷ to the determination of aniline-hydrochloride and ephedrine-hydrochloride, but obtained unsatisfactory results with various other organic bases, amino acids, ammonium oxalate and ammonium sulfate.

Koch⁷⁷ precarbonized the organic matter with hot, concentrated sulfuric

acid, then added 8 to 10 drops perchloric acid, and oxidized the organic matter in a few minutes.

The use of perchloric acid in micro-Kjeldahl digestions was discouraged by Wicks and Firminger.¹⁶⁶ It was reported that this oxidizer could cause a serious loss of nitrogen.

Perchloric Acid as an Oxidizing Agent, Solvent, and Digestion Medium

Perchloric acid may be used as an oxidizing agent for several metallic elements, especially chromium. The latter may be oxidized directly from the trivalent to the hexavalent state, in acid solution, thus obviating the use of less convenient methods such as a sodium peroxide fusion. This oxidizing ability of perchloric acid, combined with its ability to dissolve many metals or oxides, has been utilized extensively in the field of inorganic analysis.

Lichtin⁸² oxidized chromium in chrome alums to dichromate ion and determined the chromium iodometrically (after removal of chlorine).

Mixed perchloric and sulfuric acids were used by Smith and co-workers¹⁴³ in the determination of chromium in chromic oxide and chromite, and in stainless steel.¹⁴⁶

Willard and Gibson¹⁶⁹ gave directions for the determination of chromium and vanadium in chromite ores and steels. It was reported that chromium and vanadium may be completely oxidized to chromic and vanadic acid by boiling 70 per cent perchloric acid. Separation of chromium from vanadium, manganese, and iron was made by precipitation of chromium as lead chromate from a solution 1*M* in perchloric acid.

James⁶⁶ oxidized chromium in chrome-nickel and stainless steel with 70 per cent perchloric acid. Dichromate so formed was reduced with excess ferrous sulfate and back-titrated with permanganate solution. This procedure made possible the determination of nickel in the same acid solution, without prior separation.

Niebuhr and Pothmann¹⁰¹ dissolved and oxidized chromium metal by perchloric acid, prior to the determination of lead.

Bertiaux and co-workers¹² reviewed the determination of chromium in steel analysis by the use of perchloric acid and discussed the various factors which may influence the results.

Vovsi and Dobrovolskaya¹⁶¹ reported the use of perchloric acid for the determination of cobalt and iron in stellite, (a nonferrous alloy of cobalt, tungsten, chromium and carbon). The method involved oxidation of the chromium by perchloric acid, followed by distillation of the chromium as chromyl chloride, CrO_2Cl_2 . In this manner, chromium was separated quantitatively from cobalt and iron, each of which was then determined by independent methods.

Seuthe and Schaefer¹²⁵ used a mixture of perchloric and nitric acids in

the digestion of steel for the analysis of chromium, vanadium, tungsten and phosphorus, and gave procedures for the determination of these elements.

Raab¹¹² and Croall³⁰ made use of perchloric acid for the analysis of steel-work materials, alloyed cast iron, steels, chrome brick, etc.

Birckel¹⁴ discussed the use of perchloric acid for the rapid determination of silicon, chromium, nickel and molybdenum in steel and copper alloys.

Goetz and Wadsworth⁴⁹ used an equal volume mixture of 72 per cent perchloric acid and 85 per cent phosphoric acid for dissolving iron ores, prior to reduction in a Jones reductor and titration with potassium permanganate or ceric sulfate. It was reported that this procedure was less time-consuming and less subject to error than solution in hydrochloric acid.

Cădariu²² found perchloric acid to be more desirable than sulfuric acid in the analysis of silicon in silicates and aluminum alloys. Perchloric acid was also recommended for dissolving calcium oxalate prior to permanganate titration. Cădariu²³ also suggested perchloric acid for the attack of slags, dried cement slurries, portland cement, bauxite, or clay.

Turek¹⁵⁶ decomposed clay by means of hydrofluoric and perchloric acids. After conversion of the perchlorates formed into sulfates, the analysis was completed by the use of standard methods.

Norwitz and Norwitz¹⁰³ used perchloric acid for the removal of interfering substances in the electrolytic determination of lead as dioxide. Chloride, bromide, arsenic, antimony, tin and organic matter were removed by evaporating to fumes with perchloric acid, either alone or in conjunction with hydrobromic or nitric acids.

Piper¹⁰⁹ reported the use of the superior digesting properties of perchloric acid (as compared with hydrochloric acid) in the analysis of plant materials for manganese, calcium, magnesium, copper, iron and phosphorus. It was also reported that treatment of silica with hydrofluoric acid was unnecessary, after taking to fumes with perchloric acid. This was reported to be due to the fact that perchloric acid had a pronounced dehydrating effect on silicic acid. For this reason, perchloric acid has been widely adopted as a dehydrating agent in the determination of silica.^{59, 167}

Hoffman and Lundell⁶¹ made a detailed study of the volatilization of metallic compounds from solutions in perchloric acid in the presence of hydrochloric or hydrobromic acids (and from sulfuric acid solutions), and arrived at the following conclusions:

1. Chromium was satisfactorily separated from manganese (in high chromium steels) by distillation with perchloric and hydrochloric acids.
2. From solutions containing hydrochloric or hydrobromic acids, antimony, arsenic, chromium, germanium, osmium, rhenium, ruthenium and tin were quantitatively distilled in presence of perchloric acid.

3. Bismuth, boron, gold, molybdenum, tellurium, and thallium may be lost in part from hot perchloric acid (or sulfuric acid) solutions containing hydrobromic or hydrochloric acid.

In this connection, Chapman and co-workers²⁶ studied the volatilization of 37 elements from mixed perchloric-hydrofluoric acid solutions at 200°C. It was reported that appreciable quantities of boron, silicon, germanium, arsenic, antimony, chromium, selenium, manganese and rhenium were lost under these conditions. The loss was reported to be due, in most cases, to the volatilization of the fluorides of the elements.

Lundell and Hoffman⁸⁵ also discussed the effect of digestion with perchloric acid on various elements.

Perchloric acid has been used in the role of a reaction medium by Forchheimer and Epple⁴² who precipitated monovalent thallium as the dichromate from perchloric acid solution, thus separating it from trivalent thallium and iron.

Hinsvark and Stone⁶⁰ found that oxalic acid may be titrated oxidimetrically in glacial acetic acid solution by ammonium hexanitrocerate, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, and in the presence of perchloric acid. The latter was necessary in order to increase the rate of oxidation.

Stegemann¹⁴⁹ carried out a microdetermination of hydroxyproline, using chloramine T as an oxidant. The pyrrole obtained was then reacted with *p*-dimethylaminobenzaldehyde in strong perchloric acid and the red dye formed was determined colorimetrically.

Bastian and co-workers⁶ determined ferric iron in perchloric acid solution by ultraviolet spectrophotometry. An absorbance maximum at 240 $\text{m}\mu$ was found. The preferred wave length was at 260 $\text{m}\mu$ which gave less interference from other elements.

Smith and co-workers¹⁴¹ modified the Babcock test for determination of butterfat in ice cream and ice cream mixes by replacing the sulfuric acid by a mixture of equal volumes of 72 per cent perchloric acid and 95 per cent glacial acetic acid. The butterfat was insoluble in this medium, while the milk sugar and proteins dissolved, without charring.

Reviews on some of the main uses of perchloric acid in analytical chemistry have been reported by Smith^{133, 134} and Kahane.⁷⁴

Perchloric Acid in Nonaqueous Titrimetry

Many weakly basic or weakly acidic organic compounds cannot be titrated in an aqueous medium due to their failure to give sharp endpoints in water or water-alcohol mixtures, or because of their slight solubility. Many of these difficulties may be overcome by carrying out the titrations under essentially anhydrous conditions. The use of perchloric acid as the

titrating solution has been especially valuable in this connection. In general, the titrations are carried out in glacial acetic acid but other anhydrous media may be used. For the detection of the endpoint, indicators, potentiometric or high-frequency conductometric procedures may be employed.

The potentiometric titrations of various amino-compounds with perchloric acid in glacial acetic acid were discussed by Sensi and Gallo,¹²³ and by Gremillion.⁵³ Blumrich¹⁷ also used this method for the determination of amines and amine mixtures. In the case of the latter, the determination of tertiary amines was made by acrylating primary and secondary amines. The method has also been useful for the evaluation of local anesthetics,¹¹⁵ purine bases,³⁴ and pyrazolones.¹⁵⁹ Nakamura⁹⁸ determined carbonyl compounds by treating them with excess of 4-nitrophenylhydrazine in dioxane-acetic acid, then titrated back the excess with standard perchloric acid solution. Pifer and co-workers¹⁰⁸ titrated ammonium, lithium, potassium and sodium acetates potentiometrically as bases. It was reported that it was possible to differentiate between sodium and potassium acetates. Canbäck²⁴ reviewed theoretical considerations in the titration of weak bases with perchloric acid (in acetic acid) and discussed experimental conditions.

High-frequency titrations with perchloric acid in anhydrous media (acetic acid) have been employed successfully by various investigators,^{28, 91, 164} and the results were found to agree well with potentiometric and visual endpoint methods.¹⁶⁴ The standardization of the perchloric-acetic acid mixture used in nonaqueous titrations were carried out readily by means of potassium acid phthalate as the primary standard.¹²¹

In place of glacial acetic acid, other anhydrous solvents may be used to advantage in some cases. Thus, Pernarowski and Blackburn¹⁰⁷ used chlorobenzene solvent in the titration of organic bases with perchloric acid. Das and Palit³² titrated alkaloids, amino acids, aminophenols and salts of organic acids in solvent mixtures, consisting of ethylene- or propylene glycol and a higher alcohol, hydrocarbon or chlorinated hydrocarbon. Tomíček and Vidner¹⁵⁴ found anhydrous formic acid generally inferior to acetic acid. Coetzee and Kolthoff²⁷ described a method for the amperometric titration of tribenzylamine and urea with perchloric acid in a medium of acetonitrile.

Basu⁷ used a solution of perchloric acid in glycol and isopropanol for determining the molecular weight of nylon (in phenol) by end-group titration.

The perchloric acid titration method is not restricted to the evaluation of organic bases, but also permits the determination of salts of organic acids, dissolved in anhydrous media.^{28, 32, 43} A special application of this procedure to the titration of carboxylic acid salts of S-benzylthiuronium derivatives has been described by Berger.¹⁰

General surveys on the use of perchloric acid in nonaqueous acidimetry have been reported by Fritz⁴³ and Beckett and Tinley.⁹

Perchloric Acid in Oxidimetry

Perchlorato cerate anion, $\text{Ce}(\text{ClO}_4)_6^{--}$, in perchloric acid solution exhibits a relatively high oxidation potential and has found valuable uses as a volumetric oxidizing agent for many organic hydroxy-compounds. Smith¹³⁹ determined glycerol by adding an excess of perchlorato cerate solution, followed by back titration with sodium oxalate standard solution (nitro-ferroin indicator) and reported that oxidation required less time and lower temperature than was required for sulfato cerate or dichromate oxidations. The method was applicable to other polyhydric alcohols, sugars, hydroxy-acids, certain ketones, etc., as described by Smith,^{132, 140} who also discussed the generality of the method and showed many reaction mechanisms.¹³²

Use of Perchloric Acid in Electrochemical Analysis

The electrochemical deposition of copper, silver, and cadmium from dilute perchloric acid solutions has been described by Hendrixson.⁵⁸ Deposition of cobalt and nickel,⁵⁰ iron⁸⁸ and lead¹⁷⁰ has also been described. Norwitz¹⁰² has reported a general review of this field of application. It was reported⁵⁸ that the perchlorate anion was less subject to reduction than sulfate and formed no side reactions during electrolysis.

Perchloric Acid as a Deproteinization Agent

The removal of proteins from biological material is a frequent requirement in biochemical and clinical analysis, as these proteins often interfere with subsequent determinations of other substances. According to several investigators,^{52, 99, 100} perchloric acid was very effective as a precipitant for proteins, and much superior to trichloroacetic acid. In biochemical work, perchloric acid was also of value for the isolation of protein-free metabolites, amino acids, amines, peptides, etc.⁹⁹

Perchlorates as Drying Agents

Anhydrous magnesium perchlorate (Anhydrone) has found wide applicability as a general drying agent for use in desiccators, removal of moisture from air or other gases, and in chemical analysis by combustion.

The desiccating properties of magnesium perchlorate and its advantages have been discussed by Druce³⁶ and Smith.^{130, 131} The comprehensive review by Smith¹³¹ also described its preparation and properties, as well as its applications in the analysis of carbon dioxide by evolution and in combustion analysis. Mázor⁹³ made use of magnesium perchlorate in the determination of carbon, hydrogen, and fluorine in organic compounds by combustion.

Miscellaneous Applications of Perchloric Acid and Perchlorates in Inorganic and Organic Analysis

Kolb⁷⁸ suggested the use of perchloric acid in place of nitric acid in the standardization of sodium thiosulfate by copper. This method eliminated the necessity of removing oxides of nitrogen that interfere in the titration.

Smith¹⁴² recommended perchloric acid of constant composition (73.60 per cent) as a standard in acidimetry and described the procedure for its preparation.

Arndt and Nachtwey⁴ suggested pyridinium perchlorate for use as an acidimetric standard, and as a reagent for the separation of pyridine from its homologs.

Meites⁹⁴ titrated insoluble metal salts of weak acids potentiometrically with standard perchloric acid solution. From the data obtained, the solubility products of the salts were calculated. The procedure was applied to silver acetate, calcium oxalate, barium carbonate, calcium carbonate, and copper mandelate.

Mercurous perchlorate, HgClO_4 , was used by Müller and Aarflot⁹⁷ for the potentiometric determination of chlorides, bromides, iodides, cyanides, and thiocyanates and by Pugh¹¹⁰ for the determination of chloride and bromide using an adsorption indicator. The reagent has also been suggested by Pugh¹¹¹ for the volumetric determination of iron. The method was based on the reduction of the ferric thiocyanate complex to the ferrous state by mercurous perchlorate.

Sundaresan and Karkhanavala¹⁵¹ made use of ferric perchlorate as an indicator in the amperometric determination of thorium with sodium fluoride.

In the coulometric determination of certain organic bases, dissolved in acetonitrile, lithium perchlorate-trihydrate was used by Streuli¹⁵⁰ to serve as the source of water. (The water was oxidized to hydrogen ion at the anode.)

An application involving complex formation was made by Gilbert and co-workers⁴⁶ in the determination of lithium carbide in metallic lithium. The acetylene, liberated from the carbide on reacting the metal in water, was absorbed in silver perchlorate solution, and the silver-acetylene complex formed was then determined spectrophotometrically.

A micro-test for the identification of cupric ion as cupric pyridine perchlorate, $\text{Cu}(\text{C}_5\text{H}_5\text{N})_4(\text{ClO}_4)_2$, has been reported by Shead and Bailey.¹²⁶

Deniges³³ recommended sodium perchlorate as a microchemical reagent for the precipitation of potassium, rubidium and cesium, and for alkaloids.

Salvadori¹¹⁴ found that cobalt, nickel, manganese and cadmium salts

could be precipitated quantitatively by 20 per cent ammonium perchlorate in aqueous ammonia (density 0.90). As copper salts were precipitated only on long standing, from concentrated solutions, ammonium perchlorate was used to detect cadmium in the presence of copper. Also, cobalt salts were detected in the presence of cobaltammines, which were not precipitated. In general, the ammonia-metallic perchlorates had the composition $M(\text{ClO}_4)_2 \cdot n \cdot \text{NH}_3$ (for cobalt, $n = 6$; zinc, $n = 4$; cadmium, $n = 4$).

Tauber¹⁵³ reported a new color reaction for steroids, which may be useful for their quantitative estimation, especially in biological materials. It was reported that different colors were developed with various steroids on heating in chloroform solution with perchloric acid at 56°C.

Cordier²⁹ suggested the use of perchloric acid as a microchemical reagent for the detection of many organic bases, alkaloids, carbonium, oxonium, and thonium compounds.

According to Hofmann and co-workers,⁶³ perchloric acid seemed to offer advantages over picric acid for the separation of various organic compounds from resinous reaction mixtures. The authors described perchlorate separations of carbinols, ketones and amines. Hofmann and Höbold⁶² likewise suggested perchloric acid as a reagent for the detection and isolation of choline and neurine, which yielded sparingly soluble perchlorates of nitric ester of choline and brominated neurine.

A spray reagent was developed by Godin⁴⁸ for use in paper chromatography. It consisted of a mixture of one volume of 1 per cent vanillin in ethanol and one volume of 3 per cent perchloric acid in water. The reagent could distinguish polyols from cetoses, but did not detect aldoses.

An application of perchloric acid to the paper chromatography of amino acids was reported by Giri.⁴⁷ It involved the formation of different colors with perchloric acid and tyrosine or hydroxyproline. Tryptophan gave a yellow-green fluorescence with this reagent.

Schmauch and Serfass¹¹⁷ used a combination of hydrogen and perchloryl fluoride, ClO_3F , as a combustion mixture for flame spectrophotometry.

Nitrosyl perchlorate, ClO_4NO , which was readily prepared from perchloric acid and nitric acid on sodium nitrite, has been recommended as a reagent for amines and phenols by Hofmann and Zedtwitz.⁶⁴ Phenols gave characteristic colors with this reagent, but primary aromatic amines reacted violently with it.

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8. PERCHLORATES IN EXPLOSIVES AND PROPELLANTS

Inorganic Perchlorate Explosives

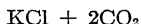
The first commercial manufacture of ammonium perchlorate was developed by Oscar Carlson, managing director of Stockholms Superfosfat Fabriks Aktiebolag, in Sweden in 1895. This product was intended for use as an ingredient in a new type of explosive for which he was granted patent coverage in 1897.^{17, 18} He pointed out that a perchlorate, particularly ammonium perchlorate, could be used as an oxygen carrier for the explosive combustion of such substances as sulfur and various organic compounds, when intimately mixed therewith. Such mixtures were found to be relatively safe to handle, but could be exploded readily by means of a suitable detonator. Most inorganic perchlorates are too hygroscopic in nature to permit their general use for such purposes, except the potassium and ammonium salts. However, these two perchlorates exhibit fundamental differences in their explosive action, as clearly described by Carlson; for example, in his British patent¹⁷ he states the matter as follows:

That an important advantage can be gained by the employment of perchlorate of ammonia instead of a perchlorate in which a metal constitutes the base is evident from the fact that in the former case gases only are formed when explosion occurs, whilst in the latter case both gases and solid substances are formed. The use of perchlorate of ammonia and carbon on the one hand, and perchlorate of potash and carbon on the other may be illustrated by the following examples:

(1) $\text{NH}_4\text{ClO}_4 + 2\text{C}$ when exploding form:



(2) $\text{KClO}_4 + 2\text{C}$ when exploding form



... In the former case ... the whole of the explosive is converted into gas, the volume of which is consequently twice as great as in the second case, and the blasting power of the explosive is thereby considerably increased.

In the few years that followed Carlson's work, perchlorates became more readily available in Sweden and in a number of other European countries, and the explosive industry, particularly in Sweden, soon began to recognize certain advantages of perchlorates over dynamite or other nitroglycerine explosives for a number of specific applications. As a result, the use of perchlorate explosives became widespread in many parts of Europe for certain types of mining and quarrying operations.

One of the outstanding features of perchlorate explosives is their greater

safety due to being much less sensitive to shock, particularly at lower temperatures where freezing seriously affects the safe handling of nitroglycerine explosives. Also, in warm climates, perchlorates are free from exudation tendencies, and they are relatively nontoxic compared with dynamite. In general, their explosive action is slower than that of nitroglycerine, but they are capable of producing a relatively greater explosive effect.⁵ Their adaptability covers quite a wide range. For example, by using mixtures of potassium and ammonium perchlorate in varying ratio, by adding sodium nitrate, or by incorporating other types of explosive materials such as nitro-organic compounds, the explosive action may be adjusted to suit the particular material to be blasted. Either hard or soft rock can be shattered into small pieces, or only broken into large blocks as in the case of the quarrying of building stone.⁵

Dynamite, on the other hand, exerts a more nearly constant effect which tends toward the shattering side. The action of perchlorate explosives seems to extend laterally more than in the case of dynamite, which is more local in its action.

The more powerful perchlorate explosives contain the ammonium salt, since all of its products of combustion are gaseous, whereas with potassium perchlorate, the K and Cl combine to form solid KCl as previously mentioned. Therefore, this latter form is more suitable for blasting the softer varieties of rock. However, HCl is normally one of the products of combustion of ammonium perchlorate. Since this is a very irritating gas and quite objectionable in mines, ammonium perchlorate explosives for use underground must be modified so as to avoid HCl formation. Various means may be used to overcome this difficulty, usually by the addition of other components such as alkali nitrates,^{16, 26, 45, 59, 79} or MnO_2 . In the case of the latter as much as 18 per cent may be required for complete suppression of HCl.¹¹

Besides the simple mixing of finely divided NH_4ClO_4 and NaNO_3 , intimate mixtures of these two salts may be conveniently obtained by double decomposition of concentrated solutions of NaClO_4 and NH_4NO_3 at relatively high temperatures such as 140°C .⁴⁵

In the case of coal mines afflicted with firedamp, it has been found that potassium perchlorate explosives are much safer to use than many other types, and have become one of the few permissible explosives under mine safety restrictions in certain countries such as England.⁵

Numerous authors have proposed various combinations of perchlorates and other oxidants as ingredients for explosives over the years. In 1909, Girard³⁸ published a review of chlorate and perchlorate explosives in which he listed the properties of some 258 compositions that had been mentioned in the literature since 1785, when C. L. Berthelot first discovered

that free oxygen could be obtained from potassium chlorate by carefully controlled heating to fusion and above.

Carbonelli in 1910¹¹ reviewed the use of ammonium perchlorate in the European explosive industry, while Alvisi² gave a brief history along with considerable experimental data on perchlorates in 1912-13. Another review, comparing the various types of explosives, was published by Kast in 1923,⁴⁸ covering developments in the industry during the preceding 50 years. In connection with ammonium perchlorate, Kast pointed out that this salt is quite normal in its behavior toward initial detonating substances, whereas NH_4NO_3 may be quite erratic.

During, and immediately subsequent to, World War I, much attention was given to perchlorate explosives. Numerous patents were issued in various countries on many formulations of perchlorates with nitrates and various nitro derivatives of such compounds as toluene, benzene, cellulose, etc. to produce composite explosives, usually in combination with other organic materials of a combustible nature.^{9, 14, 16, 23-25, 56, 58, 67, 76-78, 82, 87, 88, 90}

In a fairly recent review of explosives in the French mining industry by Médard,⁵⁷ the use of ammonium perchlorate in combination with other high explosives, such as cyclonite (RDX, or nitrated hexamethylenetetramine), is said to be gaining in interest due to the superior performance of such mixtures. This trend toward the increased use of ammonium perchlorate in conjunction with other high explosives in France is also suggested by certain French patents on such mixtures that have issued since World War II.^{29, 30}

In addition to the more usual nitro-organic explosives, numerous other types of compounds have been suggested for use with perchlorates to provide special properties. For example, both ferro- and ferricyanides may be incorporated with potassium perchlorate into mixtures that are relatively safe to handle, but which will explode readily upon simple ignition.⁷¹ Another type of ingredient for use with ammonium perchlorate consists of silicon and silicon compounds such as ferrosilicon, aluminum silicide and the alkaline earth silicides.^{16, 19, 28, 67, 82} The use of zinc in finely divided form, together with various possible combustible, nonnitrogenous carbon compounds that will not be reduced by the zinc, has been proposed in ammonium perchlorate explosives.^{59, 60, 63} Also, the addition of sulfur in small amounts may be included in some formulations.^{23, 59, 60}

The sensitivity of perchlorate explosives may be increased by small amounts of certain other compounds, present either as residual impurities from the process of manufacture, or as intentional additives: for example, a trace of cupric chloride,²¹ or 0.005 to 1.0 per cent of an alkali or alkaline earth chlorate will greatly diminish the resistance of NH_4ClO_4 to shock.^{1, 13}

However, great care must be taken not to exceed safe limits in chlorate content. Otherwise the material may become too dangerous to store or handle.¹⁵ This property is believed to be due to the formation of ammonium chlorate, a very unstable compound.

As another means of reducing the shock resistance of ammonium perchlorate explosives, Hallett⁴¹ patented the use of a small amount (not over 6 per cent) of a sensitizing agent, such as a mixture of powdered sugar and a bichromate, for incorporation in various perchlorate formulations.

Dautriche²⁶ was one of the first to point out that the bulk density of an ammonium perchlorate explosive has a considerable effect on its sensitivity to detonation, as well as upon the force of the explosion. This latter effect was later studied in greater detail by Spitalsky and Krause.⁸¹ They found that variations in the nature of the combustible ingredients had a very marked effect on the optimum charge density required for maximum brisance, or shattering effect. With some mixtures, maximum brisance was obtained when the charge was entirely uncompressed, while with others, high compression to give maximum density was needed. At low loading densities, the proportion of organic material to oxidizing agent may vary over a wide range without any appreciable effect on brisance, whereas at higher densities the brisance is decreased by increasing the organic material to the point where a deficiency of oxygen results. This effect, however, is much more pronounced with sodium chlorate than with ammonium perchlorate. According to Cook and Harris,²⁵ the "oxygen balance" of an ammonium perchlorate explosive should be between minus 4 and plus 6 per cent.

In some cases it has been found desirable to further increase the normal stability of perchlorate explosives in order to obtain still greater resistance to shock and still possess good detonating properties. This would permit their use in certain military applications: for example, as bursting charges for projectiles. Such an effect may be accomplished by compacting the charge under high compression of at least 4000 lb/sq in.,^{12, 20, 83} or by varying the type of organic materials used. For example, by compounding the perchlorates with about 17 to 18 weight per cent of paraffin wax as the organic constituent, a high degree of resistance to shock may be obtained.^{47, 65} Also, such organic materials as wood meal,^{9, 16, 19, 23, 34, 49, 67, 70, 76-78, 82} powdered cork,^{10, 79} the ground husks of certain plant seeds,⁵⁰ starch,^{34, 94} sugar,^{28, 35} gums and resins,^{4, 9, 14, 27, 39, 50, 63} various types of oils and fats,^{16, 39, 50, 79} asphalt, petroleum jelly, etc.⁵⁹ and metal soaps¹⁰ may be used to modify the bulk density, water-repellant, or caking qualities of perchlorate explosives, besides providing combustible materials for the reaction.

Another additive that has been found to increase the resistance of ammonium perchlorate to shock is MnO_2 ,¹¹ which also acts as an inhibitor of HCl formation, as previously mentioned.

The inclusion of various other materials of a more or less inert nature, such as pumice, powdered glass and infusorial earth,⁴⁶ shredded asbestos,¹⁰ NaCl and other inorganic salts^{23, 51, 52} may also be used as a method of modifying the density, sensitivity, explosive effects or products of combustion of various formulations.⁷⁵

A number of references mention the possible use of aluminum powder in perchlorate explosives,^{10, 28, 34} but in some cases it has been found that dry mixes containing metallic aluminum may become quite sensitive to mechanical shock and friction. However, in a recent patent, Streng and Kirshenbaum⁸⁴ propose to use the aluminum powder in the form of an aqueous dispersion or paste for mixing with ammonium nitrate or ammonium perchlorate. The ammonium salt should constitute from 20 to 43 per cent of the mixture while the remainder would be aluminum paste in which the ratio of Al to H_2O should be between 1.4 and 1.5. According to Kirshenbaum, such mixtures are quite safe to handle and store, but they can be satisfactorily detonated with a blasting cap or primacord. It was found that the detonation velocity of a wet mixture of this type was nearly three times that of the corresponding dry material.

A rather unusual application for a perchlorate explosive is covered by a patent issued to Frazer, *et al.*³² on producing surface explosions over large areas. This is intended primarily as a means of clearing fields of land mines. The area is first sprayed with a mixture of concentrated perchloric acid and a miscible organic liquid of low volatility, such as ethylene glycol monoethyl ether. The sprayed film is then detonated by suitable means, such as a grenade, in order to explode the mines in the area.

Despite the rather general acceptance of perchlorate explosives for specific blasting applications in Europe over the past 50 years, very little similar use seems to have been made in this country. In fact, a well-known American technological encyclopedia almost completely ignores perchlorates in a lengthy chapter on the general subject of explosives. This seeming neglect on the part of the American explosive industry is probably due to the fact that perchlorate explosives were not on the approved list for mine use and that no large explosives manufacturer in this country has seen fit to enter the perchlorate field, whereas in Europe, particularly in Sweden, most powder factories many years ago began to produce perchlorate explosives as one of their staple lines of products.⁵

Possibly another contributing factor in the above situation has been a certain amount of confusion in years past regarding chlorates and perchlorates, and a failure on the part of some authors in the explosives field

to clearly differentiate between the separate properties of these two types of compounds.³

Organic Perchlorate Explosives

Organic perchlorates, in which both the combustible material and the oxidant are already present in the same molecule, are in general much more violent in their explosive action than mechanical mixtures in which the organic material and the oxygen carrier are present as separate solid phases. A number of such compounds have been investigated as possible commercial or military explosives in the past. For example, Manuelli and Bernardini⁵⁵ patented the use of the chlorates and perchlorates of biguanide and of guanidine for use as explosives, while Rintoul and Beckett^{60, 70} covered the use of dicyanodiamidine perchlorate as a blasting explosive alone, or as an ingredient in mixtures. This compound is stated to have an explosive force equal to that of TNT, but to be insensitive to shock. When heated slowly, it begins to melt with slight decomposition at about 200°C and is completely melted at 300°C. It explodes at a temperature of 378°C. It is relatively soluble in water, but is less hygroscopic than potassium nitrate.

The perchlorates of aniline, phenylenediamines, benzidine, toluidines, naphthylamines, aminoazobenzenes, antipyrine, malachite green, fuchsin, methyl violet, pyridine, quinoline and cinchonine are all stated by Lungsgaard⁵¹ as suitable for use as explosives. Lungsgaard and Herbst⁵² have patented the use of the methylamine perchlorates, all of which are said to be stable, and, with the exception of $\text{Me}_2\text{NH}_2\text{ClO}_4$, are substantially insensitive to moisture.

The ammonium and hydrazine compounds of several bivalent heavy metal chlorates and perchlorates have been investigated by Friederich and Vervoorst³³ as possible initiating explosives for use in detonators. It was found that these compounds in general had explosive properties between those of primary explosives, such as mercury fulminate, and secondary or booster explosives, such as tetryl (tetranitromethylaniline). The chlorate compounds were found to be deliquescent and to hydrolyze rapidly. They are more sensitive than the corresponding perchlorate compounds.

The hydrazinates of the metal chlorates were mostly found to be very sensitive and unstable, particularly the copper salt. As a result they are probably too dangerous for general use, but the perchlorate-hydrazinates are much less sensitive, especially that of cadmium. A number of these latter heavy metal compounds were tested in comparison with other well-known primary and secondary explosives. The methods of testing used by these authors, together with the results obtained, are given in detail in their original series of articles.

Methylhydrazine perchlorate, plus a small amount (1. to 2.5 per cent) of combustible material, such as starch, has been proposed³⁴ as a high explosive that is said to have good stability and low sensitivity to shock. Up to 10 per cent of aluminum powder may also be added.

Vogl has patented an explosive prepared from ethylenediamine perchlorate³⁹ by forming an addition compound with picric acid or other polynitro aromatic body containing OH groups. Such explosives, as might be expected, have high detonating velocities and are said to be suitable for loading shells and for use in boosters, reinforced detonators and detonating fuses.

Perchlorates in Fuses, Pyrotechnics, etc.

The various types of fuse powders, flash compositions and similar mixtures for use in time fuses, signal flares and pyrotechnics are, in general, relatively slow burning in their action. Many of these formulations contain perchlorates or a mixture of perchlorates and nitrates as the source of oxygen for the process of combustion. For example, fusee compositions for use as railway signal flares may be prepared from potassium perchlorate, sulfur, a nitrate and carbonaceous material proportioned so as to give the desired rate of burning.⁷² Color effects may be obtained by the use of such compounds as barium or strontium salts,⁴⁰ while a small amount of potassium chlorate may also be present along with the perchlorate^{43, 73} to provide greater ease of ignition. Care must be taken, however, that no ammonium salts are present in mixtures to which a chlorate is added (see p. 136).

Other fuse powders, in which there are little or no gaseous products of combustion, may contain a finely divided metal, such as nickel, aluminum or various alloys, together with an oxidizing agent, usually a nitrate, perchlorate, or a mixture of the two.^{31, 43}

The use of a nondetonating organic perchlorate, together with an oxidizing salt such as potassium perchlorate, to form a flash composition, has been patented⁶⁶ for use as an igniter in front of the detonating charge in blasting caps. The organic perchlorate must be free from explosive groups, such as diazo, nitro or azido groups: for example, oxonium perchlorate, aniline perchlorate, and pyridine perchlorate.

Smokeless flare compositions may contain certain alkaline earth or rare earth compounds, which are heated to incandescence with a fuel composed of shellac or other combustible material, with ammonium perchlorate as the oxidant.²²

A very effective smoke-producing mixture for military or other use may be prepared from sulfamic acid and an oxidizing agent such as potassium or ammonium perchlorate.⁵⁴ The optimum mixture to give a rapid, self-sustaining reaction and a copious cloud of smoke is stated to be approxi-

mately 58 per cent sulfamic acid and 42 per cent ammonium perchlorate. The "smoke" in this case is produced by the SO_3 and HCl in the products of combustion, absorbing moisture from the air to form a dense, fog-like mist of minute droplets.

Perchlorates in the Propellant Field

Propellants in general are explosive materials which are intended to undergo decomposition *only* by a relatively slow deflagration or burning process. Unfortunately, however, they are also capable of being detonated under certain conditions, but this requires considerable energy, usually in the form of a violent shock wave, in order to initiate such a reaction. Nevertheless, they must be handled with great care, since they present a considerable hazard through the possibility of accidental ignition (see Chapter 11 on Safety Considerations in Handling Perchlorates). In the case of rockets, the danger of possible detonation of the propellant charge following ignition can be greatly minimized or entirely avoided by the proper design of the rocket components, the careful selection of ingredients and suitable processing of the propellant charge.

The first use of propellants in rockets is believed to have been made by the Chinese in the 13th century.⁹¹ Such propellants consisted of gunpowder, or black powder, as it is generally known today. This is a mixture of charcoal, sulfur and potassium nitrate and it has varied little in composition since it was first invented. However, during the latter part of the 19th century, the principle of progressive combustion was discovered and as a result, black powder was pressed into pellets, or grains of varied size depending upon the size or type of weapon in which they were to be used. The term "grain" has persisted to this day as the name applied to an individual mass of propellant charge, whether it weighs a pound or a ton.

Various advances have been made in propellant technology over the years, such as the introduction of smokeless powder for both small arms and artillery use, and more recently, liquid propellants for large rockets. With the development of various types of rockets and missiles as weapons of offense during World War II, solid propellants gained much wider use than ever before.

In more recent years, with great advances in the development of long range military rockets and missiles for defense, and the advent of space exploration, the composite type of solid propellant is assuming a role of increasing importance in these fields in competition with liquid and other types of propellants.⁹⁶ However, one of the major uses of solid propellants from the quantity standpoint has been in the *jet-assist-take-off* rocket (JATO), particularly for use with carrier based planes in the Navy. Such units are used to help launch heavily loaded planes into the air from runways or flight decks in the shortest distances possible.

Industrial applications of propellants have been small and few in number in comparison with the military and space program uses, but the recent adaptation of JATO to private aircraft⁶⁸ may soon provide a major commercial use.

In addition to applications in the rocket and missile field, various other solid propellant uses exist, such as in stud setting and oil well perforating guns, while a number of other uses are possible. For example, Hannum⁴² has patented a liquid propellant consisting of a suspension of approximately 53.5 per cent finely divided ammonium perchlorate in 46.5 per cent nitromethane for use as a self-sufficient fuel for feeding to the combustion chamber of a gas turbine, while Salzman⁷⁴ discusses the possible use of combustion gases from a solid propellant, such as a perchlorate composite, to pressurize a liquid fuel rocket. He gives data on theoretical flame temperatures and compositions of the combustion gases involved.

Rocket Propellants. More perchlorates are now used for the manufacture of rocket propellants than for all other purposes combined, and the rate of consumption for that purpose is still increasing. Most of this perchlorate is in the form of the ammonium salt, which approaches the characteristics of the ideal solid oxidizer more closely than any other commercially available compound. The closest competitors of the perchlorates are the nitrates, which are used chiefly in the form of esters, such as cellulose nitrate and nitroglycerine, and in somewhat smaller quantity as ammonium nitrate. The reasons for the prevalence of the perchlorates over their less expensive analogs can be appreciated best against a background of elementary rocket technology.

A solid-propellant rocket is a simple form of heat engine. The propellant, which is the entire source of chemical energy, comprising both fuel and oxidizer, is charged into the combustion chamber before the start of each run. As it burns it develops considerable pressure, and the products of combustion are expanded through a nozzle to accelerate them to supersonic velocity. The resulting reaction of this jet constitutes the thrust or driving force needed to propel the rocket in its flight.

Solid propellants are of two general types. In the composite propellants, the oxidizer particles are dispersed in a matrix of the fuel, while in the homogeneous or colloidal propellants, the oxidizer and fuel are not distinguishable as separate phases, and the oxidizer is usually a nitrate or nitro group attached to an organic molecule, as in cellulose nitrate, nitroglycerine, or TNT. Perchlorates are ordinarily used as the sole or principal oxidizer in composite propellants, but may be used also as a supplementary oxidizer in colloidal propellants.

Since the rocket motor is a reaction engine, as opposed to positive displacement engines, its output is measured as impulse, the product of thrust and time, rather than as work, the product of thrust and distance. If the

rocket is immobilized, so that the thrust imparts no momentum to it, the energy of the gas is entirely dissipated as heat; but if it is free to move, it receives an equal impulse in the opposite direction from the gas flow. This impulse per unit mass of propellant burned is the specific impulse. Thus,

$$I_{sp} = \frac{Ft}{W_p}$$

where F pounds of thrust are produced by burning W_p pounds of propellant in t seconds. This value is properly expressed as "lb. sec./lb.," which has the dimension of time and is frequently abbreviated to "sec." The specific impulse varies somewhat with the pressure in the combustion chamber, the design of the nozzle, and the ambient pressure. When these conditions are held constant, however, the specific impulse is a valid measure for comparing the effectiveness of various propellants, and small differences in this parameter become important in the design of long-range rockets.

The specific impulse varies directly with the square root of the absolute temperature and inversely with the square root of the molecular weight of the combustion products. It is therefore dependent on both fuel and oxidizer; but for any given fuel, the highest specific impulse is to be expected from the choice of an oxidizer with low heat of formation, high content of available oxygen, and low average atomic weight of its component atoms.

Typical specific impulses for cast composite propellants, using perchlorate oxidizers at sea level, are in the range of 165 to 210 sec for potassium perchlorate, and 175 to 240 sec for ammonium perchlorate.^{86, 95} These figures may be compared with those for black powder with a range of 50 to 140 sec, other conditions being equal.

Since the specific impulse of a propellant is dependent upon such factors as flame temperature, and the molecular weights and specific heats of the gases evolved, the range of performance of a chemical propellant is therefore limited. The maximum specific impulse to be expected from direct chemical reaction is believed to be in the upper 300's.⁸⁸ However, values of about 250 sec, seemingly, have seldom been reached with solid propellants, although according to Warren,⁹¹ values in excess of this figure may be predicted for the immediate future, possibly with the use of lithium perchlorate⁹⁸ as discussed later.

To be usable in propellants, however, the oxidizer must satisfy several other conditions in addition to high specific impulse. It must have a suitable pattern of stability versus temperature; it must be stable, nonreactive, and insensitive to shock at the highest temperature encountered previous to use, and preferably enough higher to permit the use of fuels cured

at temperatures up to 200°F; but it must decompose rapidly and predictably at some higher temperature within a hundred degrees or so from that at which the fuel is pyrolyzed. Although the reaction of oxidizer and fuel must be highly exothermic, the activation energy must be high; otherwise there would be excessive risk of accidental ignition.

High density is desirable, not only to pack the energy of the propellant into the smallest possible volume, but to maximize the volume ratio of fuel to oxidizer, thus to permit a closer approach to the composition of maximum energy without either losing the fluidity necessary for casting or risking a detonable composition.* The crystal habit should be as nearly spherical as possible, for maximum fluidity of the uncured propellant. The crystal should be wettable by the fuel phase, in order to develop good physical properties in the composite structure. The crystals should be anhydrous, nonhygroscopic, and free from phase changes within the temperature range to which the propellant may be exposed during manufacture or use. (Ammonium nitrate has a phase transition at 32°C that interferes seriously with dimensional stability during temperature changes.) Ideally, neither the oxidizer itself nor any of its decomposition products should be corrosive to metals. Finally, for military purposes, there is sometimes a preference for combustion products free from compounds that form a trail of smoke or condensed vapor.

Composite propellants may be divided into subgroups on the basis of the oxidizer used. Potassium perchlorate compositions generally have relatively high burning rates and high flame temperatures, but produce a dense smoke. Ammonium perchlorate formulations, on the other hand, have lower burning rates and lower flame temperatures, with relatively little smoke. Propellants, in which ammonium nitrate is used as the oxygen carrier, give still lower burning rates and flame temperatures, also with little smoke.⁹¹ However, the exhaust from ammonium perchlorate is conspicuous over a slightly wider range of temperature and humidity than that from ammonium nitrate, while its products of combustion are somewhat more corrosive, but for most uses these considerations are insignificant in comparison with the energy content and density, in both of which ammonium perchlorate is definitely superior to the nitrate. The difference in specific impulse theoretically attainable with a typical fuel is about 19 per cent, and as shown by the data in Table 8.1, this difference is attributable chiefly to the higher available oxygen content of the perchlorate.

Burning Rate. Rocket propellants, like gun propellants, are explosives.

* It is apparently impossible to produce a detonating composition with a non-detonating fuel unless the volume ratio of oxidizer to fuel is at least 2.85, corresponding to the ratio of solids to voids in body-centered close-packed spheres.

TABLE 8.1. CHARACTERISTICS OF AMMONIUM PERCHLORATE AND AMMONIUM NITRATE AS SOLID-PROPELLANT OXIDIZERS

	NH ₄ ClO ₄	NH ₄ NO ₃
Available oxygen content, wt %	34	20
Heat of formation, kcal/gfw	78.3	87.9
Molecular weight	117.50	80.05
Average mole wt. of combustion products ^a	24.5	21.8
Attainable specific impulse with hydrocarbon fuel ^b , lb-sec/lb	250	210
Density, g/ml	1.95	1.725
Melting point, °C	450 (decomp.)	169

^a Based on complete reaction to H₂O, CO, N₂ and HCl.

^b Estimated maximum with (C₂H₂)_n as fuel, burned at 1000 psi and expanded to 1 atmosphere.

They may or may not be high explosives, depending on their composition, but in their normal use they should burn quietly at a predictable and comparatively slow rate which depends not only on the composition but on the temperature of the propellant, the pressure in the combustion chamber, and the particle size distribution of the oxidizer phase in composite propellants.

One of the major problems in the design of solid propellant charges is to insure decomposition only at the desired rates of burning. The reaction should supply pressurized gases at the nozzle over the time interval needed for rocket acceleration without danger of having the burning reaction transformed into a disastrous explosion.

Solid propellants in rocket motors are usually fired by means of a squib and igniter assembly which should supply sufficient heat to initiate combustion of the main charge without violent shock. It is necessary only to heat the surface of the propellant sufficiently to start the pyrolysis of oxidizer and fuel, after which heat is supplied by reaction of the gaseous decomposition products. This heat transfer process determines the burning rate which is commonly expressed as the linear velocity at which the reacting surface recedes. The order of magnitude of such burning rates for most types of solid propellants is in the range of about 0.1 to a few inches per second. This may be contrasted to the rate of decomposition of a high explosive during detonation, where the velocity of the shock wave is of supersonic proportions, and may range from 2,000 to 20,000 feet per second, depending upon the particular explosive, its density, physical state, etc.⁹¹

The relationship between the burning rate, pressure, and temperature is an important characteristic of each propellant; it must be known as a basis for motor design, and must be reproduced accurately in successive

batches of propellant if the motors are to perform consistently. For most propellants, and for pressure ranges of a few hundred pounds per square inch, the relationship is adequately described⁸⁶ by the empirical equation

$$r = ap_c^n \quad (\text{I})$$

where r = linear burning (inches per second), and p_c = chamber pressure (pounds per square inch). The constants a and n then characterize the propellant.

The mass burning rate for a particular motor is

$$m_b = A_b \rho r = A_b \rho a p_c^n \quad (\text{II})$$

where A_b = area of burning surface, and ρ = density of propellant. Also, for a nozzle of constant area operating at sufficient pressure differential to produce sonic velocity at the throat,

$$m_e = k A_t p_c \quad (\text{III})$$

where m_e = mass discharge rate, A_t = cross-sectional area of nozzle throat and k = a constant (discharge coefficient).

For stable operation of the motor, the rate of gas generation must be equal to the rate of gas discharge through the nozzle. Therefore, under this condition

$$m_b = m_e$$

or

$$A_b \rho a p_c^n = k A_t p_c$$

Thus, the chamber pressure p_c at equilibrium will be given by the expression

$$p_c = \left[\frac{A_b \rho a}{k A_t} \right]^{\frac{1}{1-n}} \quad (\text{IV})$$

The constant n must have a value less than unity. Otherwise, stable operation is impossible; the pressure will continue to rise until either the casing bursts or the supply of propellant is exhausted.

Any change in the propellant burning surface or in the nozzle throat area will change the equilibrium pressure unless the two areas change simultaneously so that their ratio remains constant. This ratio, A_b/A_t or K is therefore an important parameter of motor design.

The smaller the value of n , the less sensitive the motor is to slight variations in motor dimensions that influence the value of K , or to accidental variations that influence the constant a , which is a measure of the intrinsic

burning rate of the propellant. The value of n is influenced strongly by the oxidizer composition, and there are some oxidizers that give values so high that control of chamber pressure is difficult or impossible. Ammonium perchlorate, either alone or in combination with potassium perchlorate, can be used with numerous fuels to produce propellants with n values below 0.8 that burn stably with rates between 0.2 and 1.0 inch per second at pressures anywhere within the useful range, which runs from about 200 to about 2000 psi.

One method of changing the value of K is to increase the area of the burning surface A_b through the use of grains with specially designed configurations, such as hollow or perforated grains of various shapes which may present either constant or variable burning areas as the reaction proceeds.^{95, 96}

The configuration of the grain also has an important effect on the burning stability of a composite propellant.³⁷ Using ammonium perchlorate oxidizer and a thermosetting fuel binder, an end-burning rod was found to give the most stable conditions, a tubular charge was second, while a star-perforated grain gave the most irregular combustion. Thus, by varying the configuration of the grain to obtain greater thrust, stability may possibly be jeopardized.

Unwanted changes in the exposed surface area during combustion, such as might be caused by burning down around the sides of the grain, for example, can be inhibited by suitable wraps, coatings or chamber liners, or the grain can be bonded directly to the walls of the case, or combustion chamber. The possible development of cracks in the grain due to thermal expansion can be avoided by a suitable degree of resilience and by careful design to minimize stress concentrations.

Also, in the scale-up of solid propellant grain size, the recent concept of "critical diameter," if established, may place limits on the size of any particular composition that can be safely burned without danger of possible detonation.⁹⁸ The existence of such a limitation on the grain size of ammonium nitrate propellants has been confirmed,⁹⁹ while the possible detonating conditions for large masses of other types of propellant formulations are currently under study.⁸ However, the successful static firing of a large rocket engine containing 10 tons of solid propellant has been disclosed.⁹³

The deflagration process that occurs at the surface of burning composite propellant is a complex phenomenon which has thus far defied accurate mathematical description. The continuous surface of the fuel phase is dotted with tiny islands of oxidizer. Both fuel and oxidizer are pyrolyzed by heat transmitted from the combustion zone above them, and each exposed particle of oxidizer emits a minute jet of oxygen-rich gas

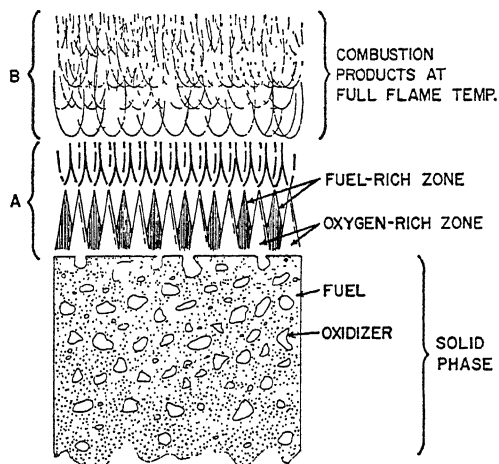


Figure 8.1. Burning mechanism.

which reacts with the surrounding pyrolysis products of the fuel as they mix in a conical reaction zone. An idealized picture of the process is presented in Figure 8.1. The result is a flame pattern somewhat like that above the grid of a Meeker burner, but with the individual jets appearing, growing, receding, and vanishing in rapid cycles as the particles of oxidizer are exposed and consumed.

The most serious attempt at mathematical analysis thus far reported was made by Martin Summerfield and his co-workers⁸⁵ at Princeton University. By means of simplifying approximations, the complex expression derived from their analysis was reduced to the form

$$\frac{1}{r} = \frac{a}{p_c} + \frac{b}{(p_c)^{1/3}} \quad (\text{V})$$

or

$$\left(\frac{p_c}{r}\right) = a + b(p_c)^{2/3}$$

Plots of (p_c/r) versus $(p_c)^{2/3}$ are found to be nearly linear. The intercept on the (p_c/r) axis yields the value of a , while b is given by the slope. There is considerable evidence that this is a better representation of the relationship than the empirical exponential expression of Equation (I), even though it purposely neglects some factors such as heat transfer by radiation.

From consideration of this burning process, it might be predicted that the burning rate will be influenced by the particle size of the oxidizer, as well as by any additive that catalyzes the pyrolysis of either the oxidizer

or the fuel. Both of these effects are known and are utilized in the development and manufacture of propellant compositions for specific uses. The burning rate is fixed approximately by the composition of the propellant, and adjusted more precisely by control of the oxidizer particle size distribution. In general, the smaller the particle size, the faster the burning. Thus, it is sometimes possible to produce a whole range of propellants of various burning rates simply by changing the particle size of the oxidizer.⁸⁶ Also, this procedure permits compensation for the effects of small random variations between successive lots of ingredients without changing the chemical composition and thus affecting other properties, such as specific impulse, in which variations may be even less tolerable than in burning rate.

In the early stages of the development of high-performance rocket motors, one of the most serious problems was the protection of the case from the high flame temperatures of the propellants. Either the case must be made thick enough to act as a heat sink, or it must be internally insulated, in order to prevent loss of strength and consequent rupture during operation. It was obvious that a case of reasonable thickness could act as a heat sink only for runs of very short duration, and that both weight and bulk would be saved by the use of a hollow propellant grain with its external surface bonded directly to the case. Such a grain could burn only at the exposed inner surface, and the case would be insulated by the propellant itself during the whole burning period. However, for a motor with case-bonded grain to withstand the temperature changes encountered in transportation, storage, and use, either the coefficient of thermal expansion of the case and the propellant must be nearly equal or the propellant must be able to withstand the strain of restraint through a temperature range of more than 200°F.

The use of elastomeric or plasticized fuels proved to be the practical solution of this problem, and the trend in composite propellants is now in that direction, especially in the high-performance motors used for large missiles and space vehicles.

Propellant Compositions. A typical ammonium perchlorate composite solid propellant might contain about 75 per cent ammonium perchlorate, 20 per cent fuel, such as a resin binder, and about 5 per cent additives intended to provide some desired effect upon physical properties, storage stability or burning characteristics.

The first successful case-bonded propellants used ammonium and potassium perchlorates as oxidizers and polysulfide rubber as fuel, and this combination is still one of the most widely used. It was obvious, however, that numerous other materials might serve as fuels in case-bonded composite propellants with perchlorate oxidizers. Some of these that have been used, with various degrees of success, are the hydrocarbon rubbers, poly-

ester resins, polyurethanes, epoxy resins, and polyvinyl chloride plastisols. For all of these except the last, a liquid monomer or prepolymer is cured by a condensation or polymerization reaction to form an elastomeric matrix surrounding the particles of oxidizer; in the plastisols, the fuel matrix is solidified by swelling and gelation of the finely divided resin with a plasticizer at slightly elevated temperature.

Many specific compositions are, of course, classified, since they are intended primarily for military purposes, but a great deal of detailed information on the design, formulation and processing of perchlorate propellants is available in the periodical literature, in certain recently published text books on rockets and rocket propellants,^{86, 91, 92, 95} and in a number of patents issued in recent years. For example, Parsons⁶¹ specifies a propellant composed of potassium perchlorate (50 to 90 per cent) in combination with a fuel composed of a mixture of asphalt to which a petroleum oil has been added to give the desired thermosetting and thermoplastic characteristics for casting and bonding to the walls of the vessel.

In the case of ammonium perchlorate as the oxidizer in combination with a similar fuel, a portion of the perchlorate may be replaced by trinitrotoluene or other nitro compounds such as pentaerythritol tetranitrate or trinitrocyclohexylamine⁶² in order to provide faster burning rates. Zaehneringer¹⁰⁰ gives some calculated data on the specific impulse of perchlorate propellants containing such fuels as styrene, polyurethane and polybutadiene acrylic acid plus aluminum powder.

Various types of synthetic resins have been proposed as fuels. For example, Hirsch *et al.*,⁴⁴ specify resins, such as glycerol sebacate resin modified with a fatty acid, or a polyamide resin such as the polymerization product of ethylenediamine with linoleic or linolenic acid.

Some organic perchlorates such as cellulose perchlorate may also find use in the rocket propellant field.⁹⁷

Mace⁵³ has patented the addition of 1 to 4 per cent by weight of a catalyst composed of a mixture of chromium sesquioxide and another metal oxide, such as ZnO , Fe_3O_4 , SnO_2 , TiO_2 , Al_2O_3 or CuO . Such an additive is said to increase the burning rate of ammonium perchlorate base propellants to make them more comparable with other types of fast burning, smokeless propellants, such as nitrocellulose, without increasing their sensitivity to shock.

Most propellant systems are oxygen-deficient, while the products of combustion are usually low molecular weight gases, depending upon the composite composition. Thus, with a typical propellant, they may be expected to be predominantly CO , H_2 , CO_2 , H_2O and N_2 . However, in view of the high temperatures involved, there may be further dissociation into simpler molecules or monatomic species.⁹²

Propellant Manufacture. The processes of manufacture for the various

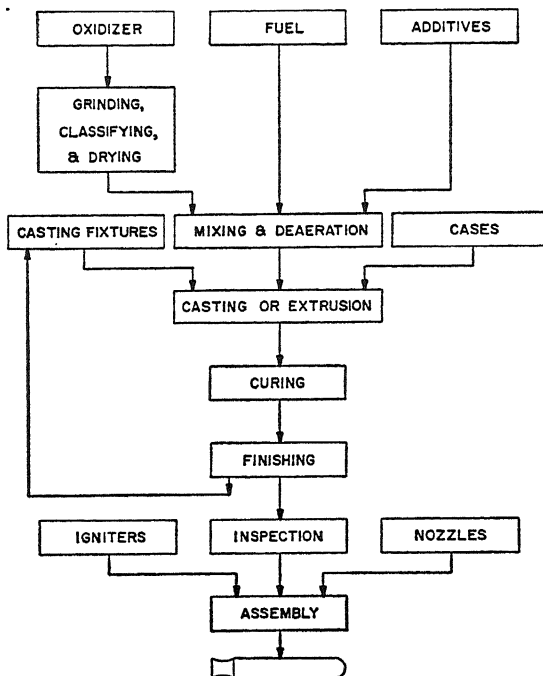


Figure 8.2. Manufacture and loading of case-bonded propellants.

composite propellants usually follow a common pattern, which varies only in details among the different compositions. This general pattern is shown in outline in Figure 8.2.

Perchlorates to be used as oxidizers are required in a range of particle sizes from about 50 mesh down to a few microns. The particles coarser than 200 mesh are preferably whole crystals with rounded corners as produced by the manufacturer; the smaller sizes are produced by grinding, usually in some form of impact mill.

Control of the burning rate in successive batches of propellant requires close attention to details in the preparation of oxidizer aggregate with a consistent pattern of particle size distribution. Because of the uncertainty of particle size measurements, especially in the sub-sieve range, the control is predominantly empirical, depending on uniformity of the starting material, constant feed rate to the pulverizer, accurately regulated mill speed, and close adjustment of critical clearances in the mill. The results of these sizing operations may be checked by sieving analysis in the size range above 44 microns and by sedimentation analysis, as with the Sharples "Micromerograph," in the range below 100 microns; but the final control is the burning rate of the propellant.

The adjustment of the particle size by grinding may be supplemented by screening of the unground perchlorate and air classification of the ground product to produce narrow cuts of more closely sized particles, which may be recombined in definite proportions to produce an aggregate in which the distribution of particle sizes is more precisely balanced.

For most types of propellant, the small moisture content of perchlorates as received is not objectionable. However, when the perchlorate is to be used with moisture-sensitive compounds, such as the isocyanates, additional drying may be necessary, and this is preferably done after the occluded moisture has been exposed by grinding.

From this point on, the process is characteristic of propellant manufacture in general rather than the use of perchlorates in particular. It should not be left, however, without some mention of the safety aspects of the operations. Although the composite propellants are classified quite properly as explosives, the chief hazard is from fire. The usefulness of propellants depends upon the fact that they burn fast and produce a hot flame, and that fact must be kept constantly in the minds of those who work with them. The burning rate is essentially the same for cured and uncured propellants. Confinement increases the burning rate, and accidental ignition in a closed vessel will inevitably cause an explosion which will rupture the vessel violently.

The compositions are not normally shock sensitive, and are usually difficult to ignite by friction or impact except in confined spaces. However, confined pinch points, such as screw threads, are especially dangerous, and any mechanical operation that does work on or close to the propellant should be done by remote control. Such operations include mixing of the propellant ingredients, trimming the cured propellant, and assembly or disassembly of loaded motors.

Lithium Perchlorate Propellants. Considerable interest has been shown in recent periodicals and other publications regarding the possible use of lithium perchlorate in rocket propellants. Its main advantage over the ammonium salt is its greater density combined with its higher oxygen content. It can thus supply nearly twice the amount of available oxygen per unit weight or over 2.2 times as much on the basis of equal volumes of the solid salts. Lithium perchlorate is also more stable and combustion temperatures appear to be higher than in the case of ammonium perchlorate. However, lithium perchlorate has a number of counterbalancing disadvantages. For example, some of the products of combustion would be solids of relatively high molecular weight (compared with H_2 , N_2 , NH_3 , H_2O , etc.), so that no spectacular increase in specific impulse may be expected, while considerable smoke would be generated. Zaehring⁹⁸ states that lithium perchlorate should put solid propellants only into the 250 to 270 sec (specific impulse) class, and that any ap-

proach to 300 sec will need drastic breakthroughs, such as in the realm of preferential and selective oxidation.

Another disadvantage of lithium perchlorate is its hygroscopic nature. At ordinary temperatures, it forms the trihydrate (see Chapter 12). However, anhydrous lithium perchlorate would probably be no more difficult to handle than ammonium nitrate in this regard, and processing of the latter under the necessary low humidity conditions is already an accepted technique. Therefore, with lithium perchlorate becoming more readily available in commercial quantities, we may look for increased interest in this chemical as a possible component for use in propellants in the near future.^{6, 7}

The Future of Solid Propellants. Despite the numerous problems facing the rocket designer in regard to this type of propellant, Zaehring predicts⁹⁸ that by 1970 all terrestrial rockets will be solid propelled. Also, the boosters for many types of space vehicles and retro-rockets for reentry will probably be using solid propellants. These may consist of either homogeneous or composite propellants, but the recent trend seems to be in the direction of the latter, with ammonium perchlorate well in the lead as the oxidant. The specifications for propellant grade ammonium perchlorate have been discussed in Chapter 6 under the method of manufacture (see p. 98).

By careful compounding of this ingredient with various types of rubber, plastic or thermosetting fuel binders, cast or extruded propellant grains of almost any desired size or shape can be produced by precision methods. In fact, a great deal of the recent success of solid propellant technology seems to be associated with mechanical "know-how" in the processing and fabrication of the grains, and in inhibiting techniques to restrict the burning to the desired areas. However, with the enormous expansion of the industry and the rapid scale-up in grain size to meet the challenge of the fast developing space age, much of this so-called "know-how" seems to be still of a more or less empirical nature. Standardization of processing techniques on sound scientific bases in many cases has not yet been achieved, and this may take time, particularly in view of the amount of secrecy involved. As Zaehring states it, "What is not classified, is in the trade secret domain."

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9. MISCELLANEOUS USES OF PERCHLORATES

In addition to the major uses of perchlorates in explosives and propellants as discussed in the previous chapter, and the many applications of perchloric acid and its salts in the field of analytical chemistry (Chapter 7), there are a variety of other important and miscellaneous uses worthy of mention. For example, perchloric acid may be used as a catalyst for esterification reactions, particularly for the acetylation of cellulose. It is used in a number of electroplating and electropolishing processes such as the bright finishing of aluminum.³⁵ Both the barium and magnesium salts have a great affinity for water, and are therefore excellent drying agents.⁶¹ Various other possible uses for perchlorates, such as in photography, medicine and chemical manufacture have been developed or suggested in recent years.^{14, 35} Details of some of these more important applications are discussed in the following sections of this chapter.

Perchlorates as Drying Agents

A comprehensive study and a collection of data on the properties and uses of perchlorates as drying agents for gases have been made by Smith⁶¹ in which he compares anhydrous magnesium perchlorate with various other types of drying agents with respect to the following:

1. Drying power (intensity).
2. Drying capacity.
3. Rate of drying.
4. Optimum temperature range for drying.
5. Optimum conditions for regeneration.

A more general study of commercial drying agents and their classification according to type is given by Bower⁹ of the U. S. Bureau of Standards, who shows in Table 9.1 a comparison of drying tests on solid reagents with humid air at 30°C in their order of increasing efficiency.

Wilson⁷³ lists the temperature-humidity conditions for sulfuric acid as a drying and humidity control agent, while the equilibrium moisture contents of various common substances under varying humidities at room temperature are reported by Wilson and Fuwa.⁷⁴

The partial pressure of water vapor over a mixture of magnesium perchlorate hexahydrate with the next lower hydrate was found⁷² to be so low, that on standing in a desiccator over phosphorus pentoxide, the mixture seemed to gradually approach equilibrium with about one-half the water of the original hexahydrate removed in 120 days. Apparently this gave rise to the notion that a trihydrate was formed. However, no single hydrate can

TABLE 9.1. DATA ON COMMERCIAL DRYING AGENTS

Drying Agent	Residual H ₂ O in Exit Air (mg. H ₂ O/L)
CuSO ₄ (anhydrous)	2.8
CaCl ₂ (granular)	1.5
Ba(ClO ₄) ₂	0.82
NaOH (sticks)	0.80
CaCl ₂ (gran. dehydrated)	0.36
Mg(ClO ₄) ₂ (mixed hy- drates eq. to 3H ₂ O)	0.031
Silica gel	0.030 (0.006)*
KOH (sticks)	0.014
Al ₂ O ₃	0.005 (0.001)*
CaO	0.003
Mg(ClO ₄) ₂	0.002
BaO	0.00065

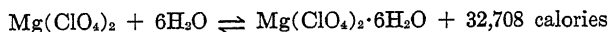
* Revised results obtained by Bower¹⁰ in a later study.

have a definite vapor pressure for a given temperature in the light of the number of degrees of freedom indicated by the Phase Rule. Also, subsequent authors have found no evidence for the existence of the trihydrate from vapor pressure and x-ray diffraction studies (see p. 41).

Willard and Smith⁷² were the first to investigate methods for the preparation of anhydrous magnesium perchlorate, while a further study of the hydrates was reported by Smith, Rees and Hardy.⁶³ The preparation of both the dihydrate and anhydrous magnesium perchlorate on a large scale for commercial use as drying agents is described by Smith and Rees.⁶²

Anhydrous magnesium perchlorate ("Anhydrone") is capable of dehydrating the hexahydrate down to the dihydrate composition at 150°C. Silica gel is practically without drying effect at 125°C, while the partial pressure of water vapor in equilibrium with aluminum oxide ("Hydralo") is too great for the dehydration of hydrated magnesium perchlorate below the tetrahydrate composition.⁶³ The use of phosphorus pentoxide above 150°C is not practical due to the increased vapor pressure of metaphosphoric acid. However, barium oxide may be used in this case.⁸

The capacity of a drying agent for absorbing moisture is measured by the amount of water reacting with a given weight of reagent, while the drying intensity is proportional to the heat of reaction evolved. This latter is, of course, also equal to the energy required for regeneration, as for example in the following reversible reaction:



However, this reaction actually takes place stepwise, first forming the dihydrate with a release of 13,509 calories, and then the tetrahydrate to

TABLE 9.2. VAPOR PRESSURE OF HYDRATE MIXTURES

Magnesium Perchlorate Hydrate Mixture	Vapor Pressure (mm Hg)
Mg(ClO ₄) ₂ —·2H ₂ O	0.56×10^{-3} (upper limit)
·2H ₂ O—·4H ₂ O	$(8.15 \pm 0.54) \times 10^{-3}$
·4H ₂ O—·6H ₂ O	$(20.9 \pm 1.1) \times 10^{-3}$
·6H ₂ O—sat. solution	81×10^{-3}

give 11,215 calories, or a total of 24,724 calories. Further hydration to the hexahydrate evolves an additional 7,984 calories.⁶³

The absolute value of the dehydrating efficiency is determined by the vapor pressure of the hydrate mixture present, while the final value is given by the mixture in which the final spent reaction compound first appears—e.g., a mixture of magnesium perchlorate tetra- and hexahydrates. Copeland and Bragg¹⁵ have measured the vapor pressures of these hydrate mixtures at 23°C, and report the values shown in Table 9.2.

However, strange as it may seem, a thorough and comprehensive study of the vapor pressures of magnesium perchlorate hydrate mixtures at varying temperatures has never been published, although this information would seem to be of fundamental importance in the use of such mixtures as drying agents. This situation in the past may have been due mainly to the fact that the vapor pressures involved are so low that most investigators were seemingly not interested in the absolute values. However, in some cases, this may also have been combined with an unfamiliarity with the Phase Rule and its value as a guide to a clear understanding of equilibrium relations in heterogeneous systems of hydrate mixtures such as these.

Anhydrous magnesium perchlorate can absorb moisture up to 60 per cent of its own weight¹ which is several times greater than with phosphorus pentoxide. It is also much better from the physical standpoint as it does not become sticky upon handling; it does not channel during use, and it contracts in volume on absorbing moisture.⁷² It is a neutral salt in contrast to acid desiccants such as sulfuric acid and phosphorus pentoxide, and it is capable of being recovered and reactivated repeatedly. However, this is somewhat difficult since the hexahydrate can be regenerated only above 400°F (204.4°C) under high vacuum. Without vacuum, the salt fuses. Therefore, because of this difficulty, together with its high cost, the use of "Anhydron" is usually restricted to laboratory purposes (see Chapter 7 on analytical uses). Its principal commercial application has been mainly as a final desiccant for gases, to remove the small amounts of moisture remaining after treatment with other cheaper but less efficient drying agents.^{32, 61} For example, in the manufacture of oxygen by the fractional distillation of liquid air, the practically complete dehydration of the

air is necessary in order to avoid periodic shutdowns of the equipment to remove "rime" (frost) deposits. This can be accomplished quite satisfactorily by using anhydrous magnesium perchlorate as a finishing desiccant after preliminary drying with solid potassium hydroxide.⁶⁰

Magnesium perchlorate for use as a desiccant may be prepared in granular form by grinding together equivalent amounts of ammonium perchlorate and magnesium oxide or magnesium carbonate, and heating the mixture at temperatures up to 350°C, or under reduced pressure to 250°C.^{58, 67} Regeneration may be carried out rapidly by heating to 140 to 250°C at pressures below 0.1 mm Hg.³⁹

Aside from its relatively high cost and difficulty of regeneration, anhydrous magnesium perchlorate seems to be one of the best all-round drying agents at present commercially available.^{1, 32, 56} However, in regard to cost and ease of handling during regeneration, these problems may be partially overcome, at least, by the use of a porous attenuating and supporting medium, such as small lumps of pumice, porous brick or asbestos impregnated with magnesium perchlorate.⁷⁶

Anhydrous barium perchlorate, marketed under the trade name of "Desicchlora," may also be used as a drying agent.^{55, 57} It is more easily regenerated, but its drying properties are not nearly as good as those of the magnesium salt previously noted. Therefore, mixtures of the two salts—for example, 1 part of magnesium perchlorate to 3 parts of barium perchlorate—are sometimes used in an attempt to utilize the good qualities of each component.^{53, 54, 59, 61, 66}

In addition to its use as a drying agent, anhydrous barium perchlorate ("Desicchlora") has been proposed as an ammonia absorbent.^{10, 55, 57}

The use of perchlorates as drying agents for organic vapors, although often used for such purposes in the past, is not recommended due to the danger of a possible explosion.⁶⁵ However, the successful use of anhydrous magnesium perchlorate has been reported³ for the quantitative removal of small amounts of organic vapors, particularly polar compounds, from inert gases, with adequate precautions (see Chapter 11).

Perchloric Acid as an Electrolyte

Electroplating and Electropolishing. Since the perchlorates of most of the heavy metals are relatively soluble, perchloric acid and its salts find many uses in metal finishing processes such as in electroplating and in etching and polishing. For example, according to Jacquet and Rocquet,²⁹ almost all varieties of iron and steel can be electrolytically polished by cleaning all oxide off the metal, which is then made the anode in a bath consisting of acetic anhydride and perchloric acid, kept below a temperature of 30°C. The cathode may be a plate of iron or aluminum, while a potential

of 50 volts and a current density of 4 to 6 amps/sq dm is recommended. Upon removal from the bath, the metal is found to be covered with a red-brown viscous layer of deposit easily removed by washing. This is believed to consist of the compound:



For aluminum polishing, Okada⁴⁷ recommends 20 per cent perchloric acid in 50 per cent alcohol, or 75 per cent perchloric acid alone at a high current density of 20 amps/sq mm.

Knuth-Winterfeldt³⁴ found that satisfactory results could be obtained with steel, cast iron and aluminum alloys at conventional voltages and current densities by using a bath containing 2 parts perchloric acid (sp. gr. 1.20), 7 parts ethyl alcohol (96 per cent) and 1 part of 2-butoxyethanol.

Heyes²⁶ reports that a comparison of electropolishing action in phosphoric-sulfuric acid and in acetic-perchloric acid electrolytes showed the latter to be superior.

Mott and Perryman⁴⁶ recommend an electrolyte containing 2 parts of perchloric acid and 7 parts acetic anhydride for use with a wide range of aluminum alloys, while Plateau *et al.*⁵¹ used 345 cc of perchloric acid with 655 cc of acetic anhydride.

Once again the reader is reminded of the explosion hazard involved in the use of perchloric acid-acetic anhydride mixtures³⁵ unless proper precautions are strictly observed (see Chapter 11).

Lead perchlorate is a highly soluble salt and the electrolytic deposition of lead from aqueous perchlorate baths has been proposed for use in both lead refining and lead plating.^{42, 43} Although the fluosilicate is used almost exclusively in electrolytic lead refining by the Betts Process,^{5, 33} while the fluoroborate and the sulfamate have found wide use in lead plating,⁷⁵ the results made possible by the use of a perchlorate bath are seemingly quite comparable with those obtained with these other electrolytes. The perchlorate bath should contain about 5 per cent lead in solution as the perchlorate and 2.5 per cent free perchloric acid. About 0.05 per cent of an organic colloid such as gelatine or peptone should also be present in order to suppress "tree" formation at the cathode.¹⁹ Current density may vary from 18 to 27 amps/sq ft. In the case of electrolytic refining, almost the theoretical amounts of corrosion from the crude lead anodes and deposition of high purity lead on the cathodes were observed, while the bath was found to show no deterioration with use provided the proper concentrations of free acid and organic colloid were maintained.

Miscellaneous Electrolyte Uses. Lash *et al.*³⁸ obtained ozone of 58 weight per cent concentration by electrolysis of 40 per cent perchloric acid with refrigerated platinum anodes held at -60 to -65°C while the batch

temperature was -56°C . The current density was 0.13 to 2.6 amps/sq dm, while the total pressure above the electrolyte was equivalent to 10 to 100 mm Hg. Current efficiency, ozone concentration and yield of ozone per kilowatt-hour were found to increase with decreasing temperature, and with increasing current density.

Another miscellaneous use for a perchlorate electrolyte is in the construction of an electrolytic voltmeter as studied by Mathers and Germann.⁴⁴ This instrument depends on the deposition of metallic mercury from an acid solution of mercurous perchlorate. The resulting metal may be easily removed and either measured or weighed and then returned to the anode for further use.

Lead storage batteries, using a mixture of perchloric acid and lead perchlorate as the electrolyte, perform better, according to Cădăriu and Schönberger,¹² than those commonly used, but silicon carbide was the only material found that proved satisfactory for anode use as a support for the lead dioxide.

Perchloric Acid as a Catalyst

Perchloric acid has been found to be quite active as a catalyst in esterification reactions, particularly for the acetylation of cellulose.³¹ This latter has been discussed by Pettinger,⁵⁰ and also by Lamborn³⁶ who claims that the catalytic action of the perchloric acid may be easily controlled by the addition of a metallic salt of hydrochloric, hydrobromic, phosphoric or sulfonic acid, or one of these acids may be used with a metal perchlorate.

Acetic esters of hydroxyethylcellulose may be prepared³⁷ by using perchloric acid as a catalyst along with zinc chloride, while Wacker⁷⁰ patented the preparation of mixed carboxylic esters of cellulose using 0.2 to 0.5 per cent perchloric acid as a catalyst.

Sorbic acid esters of cellulose may be made insoluble by polymerization, and both perchloric acid and zinc chloride²⁵ have been found to act also as catalysts for this purpose.

In the esterification of acetic acid in ethyl alcohol at 80°C , the reaction may be catalyzed by alkaline earth chlorides, bromides, perchlorates and nitrates according to Hanske.²⁰ The rate constant was found to be increased 500-fold with 0.5*N* calcium perchlorate, while with this same anion catalytic activity decreased in the order of magnesium, calcium, barium and lithium. With the calcium salts, the activity decreased in the series perchlorate, bromide, chloride and nitrate. Stearic acid was found to behave like acetic acid, both with and without catalysts. Benzoic acid alone gave no esterification in 6 weeks at 80°C , but reacted readily with a catalyst.

Catalysts are supposed to affect only the rates of reaction. However, in some cases where a reversible homogeneous reaction such as an esterification reaction is concerned, the equilibrium concentrations seem to change with the concentration of the catalyst. For example, Trimble and Richardson⁶⁹ determined the change in the apparent equilibrium constant for the reaction between ethyl alcohol and acetic acid at 30°C. They found a four-fold increase in the apparent value of this "constant" upon increasing the perchloric acid concentration from zero to over 25 mole per cent. These authors could not explain this phenomenon, but Jones and Lapworth,³⁰ who had previously noted a similar effect from the action of hydrochloric acid on this same reaction, suggested that it may be due to hydration of the hydrochloric acid, thus affecting the active concentration or molecular association of the water present. No doubt, some such similar effect may be responsible for the apparent shift in equilibrium noted in the presence of perchloric acid.

Lithium perchlorate and lithium iodide were found to be the most effective catalysts tested by Eastham *et al.*¹⁸ for the mutarotation of glucose in pyridine.

Losev and Zakharova⁴¹ investigated the relative catalytic effects of potassium, ammonium, barium and magnesium perchlorates on the polymerization of styrene at various temperatures. Magnesium perchlorate was found to be a stronger catalyst for this reaction, and the mechanism of its effect seemed to be somewhat different from that of the other salts.

According to Mathur *et al.*,⁴⁵ sodium perchlorate and acetyl chloride used together in glacial acetic acid are just as satisfactory as acetylium perchlorate or perchloric acid for use in catalyzing ring acetylation reactions. In the presence of such a mixture, certain monohydric, dihydric and trihydric phenol ethers were found to undergo catalytic ring acetylations with acetic anhydride. A 30 to 50 per cent conversion of the ethers into the acetophenones can generally be brought about at 40 to 60°C in 4 to 6 hr, depending upon the reactivity of the ethers. The acetyl group enters a position *para* to the ether grouping, and when this is not free, *ortho* substitution can also occur.

Another interesting use for a perchlorate catalyst has been revealed in the last few years in connection with a study of possible reactions for converting sunlight into chemical energy. Heidt *et al.*^{16, 21, 23, 24} have been able to establish that a simple catalytic photochemical process of decomposition can take place in water containing cerous and ceric ions, present as the perchlorates, together with an excess of free perchloric acid—a total of about 2.5 to 3.0 moles of perchlorate ion per liter. Hydrogen gas is produced by that part of the light absorbed by cerous ions in being oxidized to ceric ions, while oxygen gas is liberated simultaneously by that part of the light

absorbed in the reverse reaction of reducing ceric ions to cerous ions. By suitable arrangement of apparatus, it should be possible to produce hydrogen and oxygen in separate parts of the system where they can be collected largely free from one another.²² These could then be stored for later use as a source of energy. Although it was felt that this discovery constituted a major breakthrough in the field of utilizing solar energy, many years of research may be expected before any practical application seems possible.

In a process for the fireproofing of textiles and cellulose pulp by first soaking in sodium alginate solution and then in a solution of ethylenediamine hydrochloride,⁴⁹ the reaction may be catalyzed with hydrochloric, phosphoric or perchloric acid up to 5 per cent of the weight of the amine.

In comparing the relative catalytic actions of perchloric acid and zinc chloride for the Thiele acetylation of quinones, Burton and Praill¹¹ found that zinc chloride is not generally effective in this type of reaction, whereas in the presence of perchloric acid, the simpler quinones react rapidly with acetic anhydride.

In the polymerization of styrene in the presence of phenol, using acetic acid as a solvent and perchloric acid as a catalyst, Lilley⁴⁰ reports that the rate of reaction is proportional to the square of the perchloric acid concentration.

Painter⁴⁸ found that perchloric acid acts as a strong acid while sulfuric acid acts as a weak acid from the standpoint of their catalytic effects on the rate of anomerization of glucose penta-acetate in acetic acid-acetic anhydride solvent.

Bauer *et al.*⁴ specify the use of an acetalization agent such as an aldehyde or ketone, along with an oxygen acid, such as perchloric or persulfuric acid in the suspension polymerization of vinyl chloride. This greatly accelerates the acetalization reaction and gives a more easily centrifuged product.

Perchloric Acid and Perchlorates as Solvents for Organic Materials

As described by Hofmann *et al.*,²⁸ perchloric acid offers a number of advantages over picric acid in organic synthesis for the separation of alcohols, ketones and amines from resinous materials. The acid may be used without a solvent or the reactions may be conducted in a solvent medium such as alcohol, benzene, carbon tetrachloride, or more particularly, in glacial acetic acid. The resulting perchlorates may be decomposed, after separation, by hydrolysis, or by shaking with calcium hydroxide, potassium carbonate, etc. Apparently perchloric acid does not add to double bonds, and it has only very slight oxidizing power under the conditions employed by these authors who describe the properties of a large number of organic perchlorates prepared in this manner.

The use of 50 per cent perchloric acid as a solvent for acrylonitrile polymers in the plastics industry has been patented by Binder.^{6, 7} Such solutions are said to be much less viscous and more stable than those prepared with other solvents such as nitric, sulfuric or phosphoric acids.

Cellulose and its derivatives have been found to be soluble in certain perchlorate solutions.¹⁷ For example, absorbent cotton is insoluble in saturated solutions of sodium, calcium, magnesium and strontium perchlorates, but is dissolved by a solution of beryllium perchlorate containing 126 g of beryllium oxide and 100 g of perchloric acid per liter. The solvent action is attributed to hydrolysis of the beryllium perchlorate.

Cellulose diacetate is soluble in saturated solutions of many of the inorganic perchlorates, especially in magnesium perchlorate. No chemical action occurs during solution. For example, from 9.3 g of the acetate plus 10 cc of saturated magnesium perchlorate solution an elastic mass was obtained from which filaments and films could be formed at room temperature. Cellulose triacetate, however, was not found to be directly soluble in any aqueous perchlorate solution, either cold or hot.

The solvent action of perchlorates on cellulose fibers and their possible application in the textile industry has also been discussed by Pettinger.⁵⁰

In a process patented by Schroeder⁵² for rendering textile fabrics more crease- and shrink-proof, the fabric is impregnated with an aqueous solution containing a polymerizable alkanediol compound, such as glutaraldehyde, and a salt of an acid, chosen from a group which includes perchloric acid, as a curing agent. The impregnated fabric is then heated in the temperature range of 100 to 200°C for a few minutes to effect the curing action.

In a somewhat similar process for treating textiles to render them crease-resistant, Thomas⁶⁸ specifies the use of an aqueous solution of an epoxy resin precondensate together with a perchlorate salt as the catalytic curing agent, particularly a perchlorate of a heavy metal or alkaline earth. Approximately the same heating range may be used for curing, but in the case of aluminum perchlorate, drying may be done at 240°F (115.6°C) for 2.5 min and no further heating is necessary.

Perchlorates in Photography

Certain cationic surface-active organic ammonium salts can be converted to perchlorates² in order to effect a diminution of their surface active properties. Quaternary ammonium perchlorates of this type, having cations composed of chains of eight or more members, have been found especially useful as sensitizing agents for photographic emulsions.¹³ For example, such compounds as lauryltriethylammonium perchlorate may be used with a nonacid sensitizing dye. Similar compounds containing lipo-

philic groups of 9 to 12 member chains made up of carbon, oxygen or sulfur atoms and aromatic rings may also be used.

The preparation of lithographic printing plates in which the light-sensitive layer consists of a sulfonium perchlorate has been patented by Werner.⁷¹ Aluminum plates are coated with a compound such as an S-alkylthiodiaryl-amine sulfonium perchlorate dissolved in a suitable solvent such as ethylene glycol monomethyl ether. After drying, the plates are well suited to photomechanical printing as they show good light sensitivity and good shelf life. Suitable types of developers are specified for etching away the "nonimaged areas" of the layer, leaving the "imaged areas" as raised printing surfaces.

Other Uses

In the preparation of certain steels and ferrous alloys, it is sometimes desirable to make additions of alloying agents to a batch of molten metal without lowering the temperature. This may be accomplished by a method patented by Hilty²⁷ in which the alloying elements are mixed with an exothermic charge of material containing potassium perchlorate, sodium carbonate and silicon or ferrosilicon.

Potassium chlorate and perchlorate give off oxygen at temperatures lower than those attained in glass furnaces. Therefore, these oxidizers were used as substitutes for niter in the glass industry in Germany during World War I.⁶⁴

In view of the many unique properties of perchloric acid and its salts, numerous other uses seem possible and no doubt many of these will be developed to the point of commercial importance in the near future.

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10. BIOLOGICAL ACTION OF PERCHLORATES

Despite long industrial experience in the manufacture of sodium, potassium and ammonium perchlorates, there does not seem to be any evidence that exposure to at least these three perchlorates involves any appreciable biological hazard. This limited conclusion, however, should not be extrapolated to a supposition that the perchlorates are biologically inert or without hazard.

Investigations of the biological action of sodium and potassium perchlorates, the salts most studied, have revealed a number of interesting effects in both plants and animals. While these two compounds would be considered to be only "slightly toxic" to animals under the classification scheme of Hodge and Sterner,⁴⁰ both perchloryl fluoride and the nitrate ester of choline perchlorate would be rated as "moderately" toxic; other perchlorates may be still more toxic. The perchlorates, therefore, cover a broad range of biological activity. Unfortunately, only a very few of the many perchlorates known have been studied, and substantial gaps remain to be filled in before the details of their mode of action can be fully elucidated.

ACTION OF PERCHLORATES IN PLANTS

In 1896, Sjollesma⁷³ described damage to rye crops fertilized with Chile saltpeter, which had been occurring sporadically for a number of years. He attributed this effect to potassium perchlorate present as a contaminant in the saltpeter in amounts ranging from 0 to 6.79 per cent, varying even within the same lot (see Chapter 1 regarding the origin of the perchlorate). Sjollesma reported that $\frac{1}{2}$ or 1 per cent of either sodium or potassium perchlorate considerably delayed rye germination and produced abnormal embryos. Rye plants grown in pots containing as little as 50 mg perchlorate showed delayed growth, were stunted and bent, and had yellowed leaves. Maercker⁵⁵ noted similar effects of perchlorate-contaminated saltpeter on rye and concluded that a perchlorate content of 1.5 per cent or less could be harmful under appropriate circumstances. For example, oats were said to be damaged by 1 per cent perchlorate. Caluwe¹⁶ also studied the toxic effects of perchlorate in field experiments with rye.

Lauffs⁵⁰ investigated the effects of perchlorate on plants in greater detail. He found that small amounts of perchlorate stimulated growth and chlorophyll formation, but that the root hairs of wheat plants grown for 8 days in weak perchlorate solutions were often deformed, branched or strongly bent and thickened at the tip. An intensive protoplasmic streaming was seen in root hairs of the aquatic plant, *Hydrocharis morsus ranae*, after

3 weeks in 0.01 per cent perchlorate solution. Stiehr,⁸⁵ however, found that exposure of young wheat and rye plants to 0.2 to 1.0 per cent potassium perchlorate solutions for only a few hours had little effect on the root hairs.

Much heat but little light was added to these findings through an interesting exchange of somewhat personalized opinions between Sjollema^{74, 75} and Verweij.⁹⁰ Their discussion was principally directed to the question of whether or not perchlorate in saltpeter was actually damaging to plants in view of its low average concentration (0.2 per cent). Lauffs' comment,⁵⁰ to the effect that small amounts of perchlorate were actually beneficial although large amounts were toxic, was cited by Verweij. Sjollema⁷⁵ appears to have had the last word in this argument. He stated that: the irregularity of perchlorate content in Chile saltpeter was due to its occurrence in pockets (*Nesten*), so that some bags were toxic while others were not; plants have a variable sensitivity to perchlorate; certain suppliers had begun (in about 1892) to use an excessive recycle of the saltpeter mother liquor with a consequent increase in perchlorate content, thus accounting for the apparently sudden appearance of the damage to crops.

Vandevelde⁸⁹ also conducted some toxicological studies in which he found that the germination of the seeds of *Pisum sativum*, after soaking 24 hr in the solutions noted, was as follows: water, 98.7 per cent; 1 per cent potassium chlorate, 93.7 per cent; 1 per cent potassium perchlorate, 97.5 per cent. Potassium and sodium perchlorates both produced plasmolysis in *Allium* cells, which could be reversed by treatment with water; the cells did not appear to be harmed.

According to Alvisi and Orabona,² no chloride ion could be found in mixtures of pepsin, papain or diastase with 0.2 per cent potassium perchlorate after 1 to 6 days at room temperature. *Penicillium glaucum* reduced ammonium perchlorate but not potassium perchlorate. Experiments with beans (either the whole plant or root plus stalk) indicated that, initially, solutions of potassium perchlorate were harmful, but that eventually there was a beneficial effect attributed to the disinfecting properties of the salt. With ammonium perchlorate, the anion appeared to be decomposed through an internal reaction. The perchlorate ion was thus less stable when combined with NH_4^+ than with K^+ .

Maschhaupt,⁵⁸ returning to the problem of Chile saltpeter, found a maximum perchlorate content of 1.5 per cent, and about 1 per cent in refined saltpeter. He reported that, while the perchlorate disease of grains (*Getreide*) was due to an abnormally high content of perchlorate in saltpeter, the observed variability in the amount of damage was due to both the type of grain and the amount of perchlorate. Nevertheless, the growth-inhibiting action of perchlorate was always evident in his fertilization experiments, the plants also being more darkly colored than untreated ones. He thus substantiated the original findings of Sjollema.

Weiske⁹² also noted similar effects on the growth and germination of grains and vegetables. He found, however, that there were only slight differences when the plants were treated with the amount of potassium perchlorate, potassium chlorate, sodium iodate or sodium periodate present in the quantity of saltpeter normally used for fertilization; the difference became appreciable when 5 to 10 times this amount was used.

Since one of the effects of perchlorate on plants is a strong bending of the shoots, probably little reliance can be placed on the measurements of plant height cited by Yamasaki⁹⁶ as evidence that 0.5 per cent perchlorate solution was more toxic than 1 per cent chlorate. Cook reported that, when sprayed on plants grown in soil, perchlorate was less toxic than chlorate,²¹ although in solution culture the lethal dose was about the same (0.25 per cent) for both chlorate and perchlorate.²² Owen⁶³ described a mottling of the foliage of young tomato plants as a result of either perchlorate or chlorate poisoning, but the symptoms were not the same in both cases.

Weaver⁹¹ found that chlorate was less toxic to Biloxi soybeans than was perchlorate. Also, while chlorate was less toxic to the plants grown in water culture than to those grown in sand, the opposite was true for perchlorate. A significant difference in the effects of these two anions, noted by Weaver, was that chlorate injury began with the older leaves of the plant, while perchlorate first affected the apical meristem and younger leaves. In general, perchlorate often killed the tips of the leaflets, and the trifoliate leaves were characteristically crumpled. At 30 ppm perchlorate (the highest concentration used), the leaves failed to expand at all; at 2.5 ppm, the first trifoliate leaves had expanded normally, the second and third sets were crumpled, and the fourth failed to expand. Terminal growth was retarded and shoots arose from the axils of the cotyledons and leaves.

In a detailed study of the effects of a number of salts on young wheat plants (*Triticum vulgare* Vill.) grown in nutrient solution, Åberg¹ observed that the toxicity of perchlorate was less than that of chlorate, and that the symptoms of poisoning by these two substances were widely different. Seedlings, grown both in the light and in darkness, exhibited a marked growth depression even at a concentration of 0.1 mM perchlorate, but shoot injuries appeared only above 0.5 mM and then only in the light-grown plants. Root growth was also retarded. The typical, strong bending of the shoot noted by Sjollem⁷³ was seen in some specimens. Åberg suggested that the action of perchlorate was of a direct, physicochemical nature, in contrast to that of chlorate which he attributed to a specific mechanism involving "transformation" of the chlorate ion (possibly to hypochlorite²⁶).

Ekdahl²⁸ further investigated the effects of various salts on the roots and root hairs of young wheat plants grown in water culture. He found that the toxicity of the chlorine compounds tested decreased in the fol-

lowing order: hypochlorite, chlorite > perchlorate > chlorate > chloride. Perchlorate in concentrations of 1 mM and 5 mM had only a weak effect on root hairs in 3 to 4.5 hr, although the result was somewhat greater than that produced by chlorate. No changes were noted in either the appearance of the root hairs or the intensity of the protoplasmic streaming. Since a 1 mM solution of perchlorate did not injure the roots after exposure for 24 hr, Ekdahl concluded that it was improbable that the perchlorate could have been reduced in the cells with formation of chlorate or hypochlorite, and that the action of perchlorate was of a direct nature.

In a broad survey of the toxicity of perchlorates in animals and plants, Durand²⁴ found that poppy, lentil and flax seeds germinated almost normally in 0.2 per cent sodium perchlorate solution, but were appreciably affected in 0.5 per cent solution. *Escherichia coli* and *Staphylococcus pyogenes aureus* were unharmed by 1 per cent sodium perchlorate; development was prevented by concentrations of about 2.5 to 3.0 per cent for *E. coli*, and 7.5 to 10 per cent for *S. aureus*. For the mold, *Sterigmatocystis nigra*, development was retarded below a concentration of 1.3 per cent (1:75) perchlorate; the weight of the mycelium was considerably diminished between 1.3 per cent (1:75) and 4 per cent (1:25), and development was prevented at a concentration of 10 per cent (1:10).

It is of interest to note in passing that Heidt³⁹ has investigated non-biological photosynthesis in acidic perchlorate solutions. Perchlorate was used in this work because (1) it does not absorb visible or ultraviolet light, (2) has the smallest tendency of all negative ions in water to associate with other ions or molecules, and (3) is quite inert chemically in dilute solution. It is, Heidt states, the most inert, transparent isolationist that exists in dilute water solution.

ACTION OF PERCHLORATES IN ANIMALS

In 1868, Rabuteau⁶⁹ found that potassium perchlorate could be recovered unchanged in the urine, and he used the salt therapeutically against malaria. Sabbatini,⁷⁰ in a comparative study of the pharmacology of the oxygenated chlorine compounds, reported that, except for perchlorate, the toxicity generally decreased with decreasing oxidizing properties: hypochlorite > chlorite > perchlorate > chlorate (the same order of toxicity later found by Ekdahl²⁶ in wheat plants). The toxicity of perchlorate was attributed by Sabbatini to a sudden diminution of the potassium ion concentration (potassium-immobilization).

According to Kerry and Rost,⁴⁸ who described in detail the symptoms of perchlorate poisoning in various experimental animals, injection of from 0.015 g (minimum effective dose) to 0.030 g sodium perchlorate into frogs quickly resulted in fibrillation, twitching, and strong contraction (rigidity)

of transversely striated muscle, radiating from the site of injection. The central nervous system was affected, as evidenced by greatly increased excitability of the reflexes even in decerebrated animals, and the heart was gradually paralyzed. The symptoms were less severe when the perchlorate was administered orally: although a dose of more than 0.05 g produced rigidity without the intervening muscular activity, recovery was complete when less than 0.15 g was administered.

In rodents (rats, mice, guinea pigs), sodium perchlorate produced increased reflex excitability, convulsions and tetany, often with opisthotonus. The symptoms appeared within 10 min after subcutaneous injection of 0.1 g perchlorate in rats, while 0.22 g resulted in death after 10 hr. A subcutaneous dose of 0.025 g was lethal for mice, and 1.35 g for guinea pigs; 2.9 g given orally proved fatal to a guinea pig in about 6 hr. Rabbits were unaffected by 0.4 g subcutaneously, 1.35 g intravenously (no change in blood pressure), or feeding of 1.0 g/day for some time (duration not stated). However, a single oral dose of 1.5 g in 4.5 per cent solution produced death in about 3 hr; numerous dot-like hemorrhages were found in the cecum on autopsy.

A pigeon, injected (partly intramuscular, partly into the crop) with doses of up to 0.22 g perchlorate, developed only mild symptoms but died in 18 hr. A dog, unaffected by the subcutaneous injection of 1.5 to 2.2 g, developed slight paralysis after oral administration of 4.40 g in 5.5 per cent solution. Subcutaneous injection of 1.5 to 2.2 g in cats produced definite disturbances. Vomiting followed (in 30 min) an oral dose of 2.75 g (in 50 ml of solution); a later intravenous injection of about 2.5 g (in 45 ml of solution) in the same animal produced slight paralysis, spastic rigidity, twitching and subsequent reflex excitability with tetany, clonic convulsions and death (in about 20 hr).

Part of the perchlorate administered intravenously to a rabbit was recovered unchanged in the urine by separation as the tetramethylammonium salt.⁴³

Messini used the isolated gastrocnemius of the frog to study further the pharmacodynamic effects on striated muscle⁵⁹; the action on smooth muscle was examined with guinea pig and cat uterus, the lower part of the cat esophagus, and the frog stomach.⁶⁰ The muscle contractions produced by addition of sodium perchlorate to the perfusion fluid were relieved by amounts of potassium chloride smaller than those known to inhibit muscle excitability, and, conversely, increased muscle tone from high doses of potassium chloride was diminished by sodium perchlorate. On the other hand, calcium and magnesium chlorides relieved perchlorate contractions only in doses larger than those known to suppress muscle excitability. The contraction-relaxation sequence from excess perchlorate ion and potassium

ion, respectively, could be repeated on muscle washed with sodium chloride solution.

In agreement with Sabbatini,⁷⁰ Messini attributed these phenomena to a disturbance of potassium ion equilibrium within the muscle, not by simple precipitation of potassium as the perchlorate, but rather by reduction of its thermodynamic activity. The equilibrium is restored by addition of small amounts of potassium chloride.

Cartolari²⁰ confirmed the reciprocal antagonism of perchlorate and potassium on the isolated frog heart. The action of perchlorate was similar, although more intense, than the effect of a potassium deficiency in the perfusion fluid. Small doses of perchlorate diminished the tone of the heart and the amplitude of its pulsations, while large doses produced transitory, grouped pulsations. Spagnol⁸² concurred that perchlorate produces a decrease in the potassium ion concentration in the blood with a consequent change in the Ca:K ratio. He found that injection of sodium perchlorate into animals caused a depression of the parasympathetic-vagal system; high doses produced complete paralysis. The sympathetic system became hyperexcitable, with excessive sensitivity to adrenalin.

Eichler,²⁵ however, contended that the symptoms of perchlorate poisoning in frogs, which generally resembled the effects of thiocyanate, were more akin to those from an excess rather than a deficiency of potassium. Furthermore, he reported that perchlorate-poisoned frog hearts were cured by addition of calcium ion, but not by potassium. Cartolari²⁰ strongly contested this conclusion on the basis of his own observation that addition of perchlorate was beneficial rather than harmful to the frog heart poisoned by potassium chloride.

Boehm^{11, 12} who investigated the reaction of sodium and potassium perchlorates on transversely striated muscle (frog sartorius), noted the occurrence of two contractions: a transient first contraction immediately following immersion in the isotonic test solution and gradually diminishing during 5 to 10 min; then a second one, beginning after the lapse of several minutes, which reached a maximum in about 15 min and lasted for more than an hour. Calcium chloride largely prevented the first contraction and delayed completion of the second contraction. The effect of previous curarization of the muscle was not clear-cut, but addition of novocaine after the perchlorate completely suppressed the second contraction. The great similarity of the effects of perchlorate to those produced by fluoborate was attributed by Boehm to the similar structure of the two anions; fluosulfonate, however, failed to cause more than an initial slight contraction. Boehm related the contracting action of perchlorate and fluoborate to precipitation of albumin within the muscle.

Both Eichler²⁵ and Boehm¹² placed perchlorates beyond thiocyanates

in the Hofmeister lyotropic (anion) series,⁷⁹ in which anions are arranged in an order related to the diameter of the ion and the interaction between the ion and the dipoles of the water molecules.

As mentioned above, Kerry and Rost⁴³ found that the oral administration of 1.5 g sodium perchlorate to a rabbit caused convulsions and death in 3 hours. Kahane⁴² also explored the toxicity of sodium perchlorate in rabbits and fish. In the rabbit, intravenous injection of 89 mg/kg body weight (0.5 ml, 50 per cent solution) had no effect, but 370 mg/kg body weight (2 ml, 50 per cent solution) produced prostration and total paralysis of the hind quarters lasting 10 to 15 min. Intracardiac injection of 179 mg/kg body weight (1 ml, 50 per cent solution) also resulted in temporary paralysis of the posterior. No methemoglobin was found on spectroscopic examination of the blood, showing that reduction of perchlorate to chlorate did not occur (compare effects of perchloryl fluoride). Repeated intravenous injections of a total of 0.55 g sodium perchlorate (200 mg/kg) during 8 days caused diarrhea; on autopsy, there were no changes in the heart, kidney or intestines, but the liver showed numerous areas of caseation. Subcutaneous, then intramuscular, injection during 12 days of a total of 3.95 g (1795 mg/kg) perchlorate resulted in diarrhea, emaciation, necrosis of the tissue at the injection sites (4 injections of 10 per cent solution, 5 of 50 per cent solution) and, after 8 days, death. Here, also, extensive caseation of the liver was noted.

Goldfish were not affected after 3 days in 0.1 per cent sodium perchlorate.⁴² At higher concentrations, the results were as follows:

Per cent NaClO ₄	Deaths/Total	Exposure (hr)
0.2	1/5	24
0.5, 1	2/5	24
2, 4	3/3	10

Again, Kahane found no evidence of reduction of perchlorate to either chlorate or chloride.

Durand²⁴ reported signs of paralysis in a rabbit sacrificed 2 hours after oral administration of 2 g sodium perchlorate, a dose which Eichler⁸ had found to be fatal. Lest the amounts of perchlorate cited be considered as being precise, it may be noted that there is some discrepancy in Durand's statements about the toxic effects of perchlorate injected intramuscularly in the rabbit. On the one hand, he referred to a dose of 0.5 g as harmless but 1 g as toxic and fatal; he then described in detail the symptoms resulting from injection of 0.5 g (263 mg/kg), including muscle contraction, paralysis, tetany, and death in 4 days. Autopsy of the latter animal revealed the following: minor local lesions and congestion at the site of

injection, and hepatization of the lungs; the sciatic nerve, kidney, intestine, liver and brain were intact.

Tadpoles immersed in perchlorate solutions of various concentrations were affected after 48 hr in 0.1 per cent solution (3/5 dead); all (5/5) were dead after 36 hr at 0.2 per cent and 0.5 per cent, after 24 hr at 1 per cent and after 12 hr at 2 per cent. Leeches similarly treated were unharmed after 5 days in 0.5 per cent perchlorate; 2/3 were dead after 2 days at 1 per cent, 5/5 after 24 hr at 2 per cent, and 5/5 after 1 hr at 4 per cent.

Durand²⁴ also extended the studies of Rabuteau,⁶⁹ Kerry and Rost,⁴³ and Eichler²⁵ on the elimination of perchlorate in the urine. Eichler²⁵ reported that 75 per cent of the potassium perchlorate taken orally by man was eliminated in 24 hr, and up to 95 per cent in 72 hr, with a total recovery of 85 to 95 per cent. Durand²⁴ made the following observations of the fate of 0.784 g sodium perchlorate in 100 g water ingested by a normal human subject:

1. Perchlorate appeared in the urine 10 min after ingestion.
2. The maximum concentration of perchlorate occurred at about the third hour. The rate of elimination was: 30 per cent in 3 hr; 50 per cent in 5 hr; 85 per cent in 24 hr; 95 per cent in 48 hr.
3. All of the perchlorate ingested (within experimental error) was recovered. There was no chemical evidence of reduction of perchlorate to chlorate.

Distribution of sodium perchlorate throughout the rabbit body was also rapid²⁴; it was found in all of the organs tested within 20 min after intravenous injection. Although the concentration in the same organ varied somewhat, depending on the route of administration (intravenous, intramuscular, oral) and on the time allowed for distribution (20 to 130 min), three broad categories were suggested by Durand from the data of three experiments:

1. Average concentration less than 100 mg sodium perchlorate/100 g tissue: heart, liver, lungs, kidneys, brain, blood, gastric mucosa, muscle, bone, testes (one experiment).
2. Average concentration 100 to 200 mg/100 g tissue: spleen, gall bladder, intestinal mucosa.
3. Higher concentrations (per 100 g tissue): ovaries, 445 mg; adrenal glands, 900 mg; urine, 640 mg.

It is unfortunate that the toxic symptoms and treatment of chlorate poisoning as given in the sixth edition of Sollmann's "Manual of Pharmacology"⁷⁷ are incorrectly attributed by Van Arsdell⁸⁷ to perchlorate. The same description of the toxic effects of swallowing large amounts of chlorate has been repeated in the eighth edition of Sollmann's work.⁸¹ Actually,

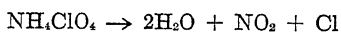
in many years of large-scale industrial production of various perchlorates—particularly the sodium, potassium and ammonium salts—no report has been found of any case of perchlorate intoxication.

The so-called irritating effect of perchlorates may also be in error. Except for the well-known corrosive (biological) or irritating effects of perchloric acid, no published information has been found which would confirm the following statement by Sax⁷¹: "Perchlorates are unstable materials, and are irritating to the skin and mucous membranes of the body whenever they come in contact with it. Avoid skin contact with these materials."

Schwartz⁷² also lists perchlorates in a table of known primary skin irritants, but without any supporting data. Possibly the irritant effects of the alkali metal chlorates have been incorrectly attributed to the alkali metal perchlorates, and thence, by generalization, extended to all the perchlorates.

Because of the current interest in perchlorates as oxidizers in rocket propellants, some mention should be made of the possible hazard from inhalation of their combustion products. Feinsilver *et al.*³² have investigated the inhalation toxicity in rats and mice exposed to the discharge gases of propellant mixtures containing various amounts of perchlorate; some of these compositions also contained sulfur. The discharge gases from all of the propellants contained carbon monoxide and hydrogen chloride; in addition, the mixtures containing sulfur discharged sulfur dioxide and hydrogen sulfide. All of these combustion products caused severe respiratory damage. The test animals which were dead or sacrificed immediately after exposure exhibited pulmonary edema, pulmonary hemorrhage, tracheitis and pneumonitis (with and without necrosis), and combinations of these. Extrapolation of the data by the authors indicated that a man exposed to the gases from a 400 g charge in a 20 m³ chamber would be endangered in 30 to 60 min.

Although not mentioned by Feinsilver *et al.*³² as occurring in their study, nitrous oxide, N₂O, nitric oxide, NO, and nitrosyl chloride, NOCl, have been found among the products of the thermal decomposition of ammonium perchlorate (see Chapter 3). In patenting the use of ammonium perchlorate explosive compositions, Carlson¹⁸ stated that the decomposition on explosion proceeded according to the equation:



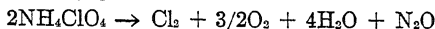
With 3.5 per cent added carbon, he formulated the decomposition as:



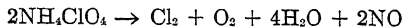
More reliable information has been provided by Bircumshaw and co-workers^{8, 9, 10} who reported that the main products of the thermal decom-

position of ammonium perchlorate are:

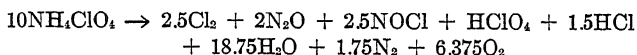
below 300°C



above 300°C



At higher temperatures, both nitrous and nitric oxides are formed, but the nitric oxide reacts with the chlorine and is analyzed as nitrosyl chloride. In a run at 420°C, gas analysis of the products gave the following results⁶²:



The corrosive action of perchloric acid is discussed later in this chapter. The hazards from inhalation of hydrogen chloride and chlorine are well known and need not be elaborated. Nitrosyl chloride is included among the respiratory irritants.²⁸ In a detailed review of the toxicity of the oxides of nitrogen, Gray⁴⁰ notes that nitrous oxide, N_2O , is considered to be dangerous only in high concentrations (approaching 90 per cent), and then principally from anoxia; nitric oxide, NO , appears to be only about one-fourth to one-fifth as toxic as nitrogen dioxide, NO_2 . Nevertheless, the possibility should not be excluded that a hazard from nitrogen oxides may occur when ammonium perchlorate is decomposed under appropriate conditions.

Effect of Perchlorate on the Thyroid Gland

It has been demonstrated that thiocyanate interferes with the collection and concentration of iodide ion in the thyroid gland.^{7, 88} The separate process of hormone synthesis, in which iodide is combined with tyrosyl groups, is prevented by thiourea and related compounds such as propylthiouracil, methylthiouracil, and 1-methyl-2-mercaptoimidazole.^{5, 6, 41, 53, 84} Wyngaarden, Wright and Ways⁹⁵ found that the monovalent anions perchlorate, chlorate, hypochlorite, periodate, iodate, biiodate and nitrate share with thiocyanate the properties of inhibiting collection and interfering with retention of iodide in the thyroids of rats chronically treated with propylthiouracil. The blocking effect of perchlorate on the thyroid appears also to extend to other iodide-concentrating mechanisms of the animal body.³⁷

Perchlorate, periodate, iodate and chlorate produced the quantitative discharge of iodide from rat thyroids, but only perchlorate did so within 15 min.⁹⁵ In this respect, perchlorate was about 10 times more effective than thiocyanate, and approximately 300 times more than nitrate, in discharging radioiodide; hypochlorite and biiodate were intermediate in potency. Investigation of the ability of these substances to prevent the

accumulation of iodide showed them approximately to parallel their iodide-discharging action, with perchlorate again the most effective. Rats treated with perchlorate for 17 days developed hyperplastic, colloid-depleted, low-iodine goiters. The changes were as marked as those resulting from ingestion of propylthiouracil.

Halmi and Stuelke³⁶ reported that, while subcutaneous injection of 100 mg or more of sodium perchlorate prevented active uptake of I^{131} by the thyroid glands of rats treated with propylthiouracil, all of the trapped I^{131} was not discharged if the perchlorate was given after I^{131} administration. The longer the interval between the injection of I^{131} and sodium perchlorate, the smaller the amount of I^{131} which could be discharged. The non-dischargeable I^{131} did not appear to be bound to thyroglobulin.

A study was made of the effects in the rat of increasing quantities of iodide, thiocyanate, perchlorate and nitrate on the ability of the thyroid gland to concentrate radioiodide.⁹⁴ All of these anions produced a marked reduction of the radioiodide concentration gradient between thyroid and serum. Here, again, perchlorate was the most potent anion, and nitrate the least; iodide and thiocyanate were intermediate and of approximately equal effectiveness on a molar basis.

As a result of further animal studies, Krüskemper and Kleinsorg⁴⁸ suggested, contrary to the opinion of the group at the Massachusetts General Hospital,⁹⁵ that perchlorate interferes with the synthesis of thyroxine. They reported that potassium perchlorate reduced the respiration of the liver in normal rats⁴⁸ and mice,⁴⁴ but there was no effect on tissue respiration *in vitro* and no peripheral antagonism to thyroxine. In hypophysectomized rats, potassium perchlorate suppressed the metabolic increase produced by thyrotropic hormone, and the enlargement of the thyroid gland found in normal animals did not appear even at a dosage level of 250 mg/kg/day.⁴⁴ The effects on metabolism and weight of the thyroid gland produced by administration of 250 mg/kg/day of potassium perchlorate for 14 days were the same as from 100 mg/kg/day of methylthiouracil; there were no toxic effects. The results in mice were similar: doses of 100 mg/kg/day perchlorate alone decreased liver respiration and increased thyroid weight, although the effects of simultaneously injected thyroxine on metabolism and thyroid weight were not altered.⁴⁴ Breslavskii and Simon¹³ obtained qualitatively similar results in rats; they reported, however, that the uptake of radioiodide and the increase in weight of the thyroid glands were markedly smaller in animals treated with potassium perchlorate than in those receiving equimolar doses of methylthiouracil.

In a study of the effect of thyroxine and antithyroid substances (potassium perchlorate and methylthiouracil) on the serum protein in rats, Kleinsorg and Krüskemper⁴⁵ noted that thyroxine (3 mg/kg/day for 10

days) decreased the serum protein from 6.93 gram-per cent to 5.61 gram-per cent. There was no change when potassium perchlorate (100 mg/kg/day) was fed simultaneously, but the albumin decreased by 21.5 per cent and the globulins by 15 per cent (α , β and γ at the same rate). Potassium perchlorate alone, fed at 100 or 250 mg/kg/day, raised the β -globulin content by 68 per cent in 14 days, and 94 per cent in 28 days, while the albumin/globulin ratio was lowered from 1.8 to 1.17. Methylthiouracil, at 100 mg/kg/day, raised the β -globulin by 79 per cent and lowered the albumin/globulin ratio to 1.37. In the latter two cases, there was very little, if any, change in albumin content, but total protein increased from 7 to 15 per cent.

Oral administration of 3 to 500 mg doses of potassium perchlorate to thyrotoxic (Graves' disease) human subjects pretreated with 1-methyl-2-mercaptoimidazole resulted in the rapid release of previously accumulated iodide from the thyroid.⁸³ No toxic effects of perchlorate were seen at this dosage level (total of not more than 600 mg). Like thiocyanate, perchlorate inhibited the accumulation of I^{131} ; Brügél¹⁵ found that the amount taken up was reduced to less than 1 per cent of the normal amount. The period of inhibition after a single dose of 100 mg perchlorate was about 6 hr,⁸³ within which time, as demonstrated by Durand,²⁴ a little more than half of the perchlorate administered would have been eliminated in the urine. Subsequently, hyperthyroidism was also successfully controlled in 24 patients treated with oral doses of 200 to 400 mg potassium perchlorate every 8 hours.³³ Symptoms improved and the basal metabolic rate and serum concentration of protein-bound iodine returned to normal. The only toxic manifestations were seen in two of the patients who developed irritation of the gastrointestinal tract, which the authors felt might have been due to the perchlorate. There were no significant changes in the formed elements of the blood and no evidence of liver damage, although some patients were treated for as long as 52 weeks. The authors concluded, therefore, that potassium perchlorate was an effective antithyroid agent in the preoperative continuous treatment of thyrotoxicosis, and of particular value in those patients who may be sensitive to or fail to respond to drugs of the thiourea group or iodide.

Confirmatory results in 15 hyperthyroid patients were obtained by Kleinsorg and Krüskemper.⁴⁶ At oral dosage levels of 0.8 to 1.2 g potassium perchlorate per day for up to 4.5 months, the basal metabolism fell to nearly normal, body weight increased, and blood cholesterol increased to normal.⁴⁷

Effects of Perchloric Acid

The extensive use of perchloric acid as an analytical reagent has been discussed in Chapters 2 and 7. The cold 70 to 72 per cent aqueous solution

has no oxidizing power; it acts as a strong acid and exhibits the reactions of the hydrogen ion. The hot, concentrated acid, however, is a strong oxidizer and dehydrating agent. Like other strong acids, perchloric acid in the form of liquid, mist or vapor is highly corrosive to the skin, eyes and mucous membranes. The amount of damage will depend upon the concentration, temperature, and duration of contact.

Perchloric acid is considered to be a primary skin irritant: i.e., a substance that causes dermatitis by direct action on the normal skin at the site of contact if it is permitted to act in sufficient concentration or quantity for a sufficient length of time.^{66, 72} A primary skin irritant may also be a sensitizer: i.e., a substance that does not necessarily cause demonstrable skin changes on first contact, but effects such specific changes in the skin so that, after 5 to 7 days or more, further contact (of the same substance) on the same or other parts of the body will cause dermatitis.^{66, 72} While no cases of sensitization specifically attributed to perchloric acid appear to have been described, the possibility that this may occur in certain individuals should not be excluded.

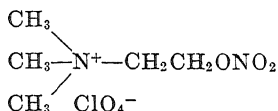
Since perchloric acid is not very volatile, the types of injury most likely to occur in industry are irritation of the respiratory tract through inhalation of the mist or spray, and severe burns of the eyes and skin through contact with the liquid. No reports of accidental ingestion of perchloric acid have been found in the literature.

The simple precautions to be followed in handling perchloric acid are briefly stated in a number of publications.^{4, 31, 38, 56, 61} Like other strong acids, perchloric acid should not be pipetted by mouth suction. Since protection of the eyes and skin is essential, at least chemical safety goggles and rubber gloves should be worn. Personnel handling quantities of perchloric acid should be provided with chemical safety goggles, rubber gloves, rubber sleeves, rubber apron, and rubber safety-toe boots or shoes. Deluge showers and eye-washing fountains should be provided in all working and storage areas. Clothing contaminated with perchloric acid is highly flammable and should be removed and washed thoroughly with water. In case of accidental contact with perchloric acid, the skin or eyes should be flushed immediately with large quantities of water for at least 15 min; any contact with the eye should receive prompt medical attention.

The requirements for packaging, labeling and shipping perchloric acid are discussed in Chapter 11.

Effects of Nitrate Ester of Choline Perchlorate

The pharmacology of the nitrate ester of choline perchlorate, has been examined by Carr *et al.*¹⁹ This compound is a stable, white, crystalline ma-



terial, melting point 188 to 189°C, easily recrystallized from water. The solubility in water is 0.82 g/100 ml at 20°C; the pH of a 0.1 per cent solution is between 6 and 7.

Two drops of a 1 per cent solution of the nitrate ester of choline perchlorate dropped into the rabbit eye caused strong pupillary constriction (miosis) within 10 min; this was antagonized by atropine. In comparison, choline and nitrosocholine do not produce miosis. At a concentration of $1:10^5$, the depressor activity was about one-half that of acetylcholine; this effect was obliterated by atropine but not by cholinesterase. The contracting effect in vitro on the frog pylorus was greater than that from acetylcholine ($1:2.5 \times 10^5$). Injection of 1 to 40 mg/100 g body weight in rats produced chromodacryorrhea ("bloody tears") within 1 min which was obliterated by intraperitoneal injection of atropine sulfate (10 mg/100 g). The LD_{50}^* (1 hr) by intraperitoneal injection in the rat was found to be 25 mg/kg body weight; the nitrate ester of choline perchlorate is, therefore, approximately 10 times more toxic than acetylcholine. The deaths from its administration were much more prompt than those caused by acetylcholine; convulsions, which occurred within 3 min (at lethal doses) and lasted no longer than 1 min were clonic and characterized by marked emprosthotonus.

Effects of Perchloryl Fluoride

Perchloryl fluoride, ClO_3F , is included in this review of the biological action of perchlorates since the infrared vibrational,⁵² rotational⁵⁴ and microwave⁵¹ spectra support the perchlorate type of tetrahedral structure with the fluorine and oxygen atoms bonded directly to chlorine. It appears to be the first perchlorate to have been subjected to the current systematic technique of acute toxicity screening in laboratory animals which has proved so valuable in establishing modern industrial hygiene, precautionary labeling and shipping standards.^{17, 27, 40, 57, 64} The chemical and physical properties of perchloryl fluoride are discussed in Chapter 5.

Greene *et al.*³⁵ and Kunkel⁴⁹ have reported the effects in rodents and dogs of single and repeated exposure to perchloryl fluoride. The gas was metered from a cylinder at room temperature into a dynamic exposure chamber. In rodents exposed for a single 4-hr period, the LC_{50}^\dagger was found

* LD_{50} = amount which kills 50 per cent of a group of test animals.

† LC_{50} = concentration of a gas which kills 50 per cent of a group of test animals exposed for a given period of time.

to be 385 ppm (1610 mg/m³)* for male rats and 630 ppm (2640 mg/m³) for female mice. Most of the deaths occurred during exposure and none later than 2 days after exposure.

Dogs similarly exposed for a single 4-hr period to 224 ppm and 524 ppm perchloryl fluoride developed cyanosis and hyperpnea. At concentrations of 451 ppm (for 4 hr) and 622 ppm (for 2.5 hr), the dogs became seriously ill, showing cyanosis, hyperpnea, convulsions and emesis; these animals died unless treated with methylene blue after exposure. All of the dogs developed methemoglobinemia which disappeared within 1 to 5 days after exposure.

In rodents repeatedly exposed for 6 hr/day, 5 days/week to 185 ppm perchloryl fluoride, the mortalities were 10/10 guinea pigs in 3 days, and 18/20 rats and 20/29 mice after 7 weeks.³⁵ All the animals showed slight cyanosis and polypnea, with occasional cases of exophthalmos. The rats, which were examined in greater detail, were found to have developed methemoglobinemia during the first week of exposure, but after the second week methemoglobin and hemoglobin values approached normal levels. When these subacute exposure experiments were repeated for 5 weeks at a concentration of 100 ppm, 1/20 rats and 10/10 guinea pigs died within 2 weeks; the blood picture was essentially the same as that found at 185 ppm.⁴⁹

In addition to pulmonary irritation, methemoglobinemia, and a decrease in total hemoglobin in both rodents and dogs, the authors also report³⁵ an increased fluoride content of the blood, hemosiderosis (indicating hemolysis during exposure) and increased hematopoietic activity (the spleens were considerably enlarged). Other investigators are cited as having observed similar effects with larger quantities of perchloryl fluoride,^{14, 68} or more severe effects at the same exposure level using static exposure chambers.⁶⁸ Exposure of rats and monkeys to as little as 40 ppm for 3 months produced enlarged spleens and lungs with some evidence of red cell destruction, although there were no external signs of damage.⁶⁸

Despite its perchlorate structure, the physiological activity of perchloryl fluoride thus appears to be more like that of chlorate than of perchlorate with respect to the formation of methemoglobin. The oxidation of hemoglobin (ferrous iron) to methemoglobin (ferric iron) can be accomplished in vitro by a number of oxidizing agents, but only chlorate is said to do so in vivo.⁷⁸ The typical formation of methemoglobin and the destruction of red corpuscles by chlorate are cited by Sollmann.⁸⁰ However, Eichler,²⁵ Kahane⁴² and Durand²⁴ found no evidence of methemoglobin formation after administration of sodium or potassium perchlorate.

*At 25°C and 760 mm Hg:

$$1 \text{ ppm} = \left(\frac{\text{mol. wt.}}{24.45} \right) \text{ mg/m}^3$$

Pennsalt Chemicals Corporation⁶⁷ states that no injuries have occurred during a number of years of laboratory and plant experience with perchloryl fluoride. A tingling sensation is said to be felt on exposed skin surfaces, but the gas is not irritating to the skin or eyes. Frostbite can, of course, occur from contact of the skin with the low-boiling (-46.8°C) liquid.

It has been pointed out⁶⁷ that, using $\text{LC}_{50} = 385 \text{ ppm}$ (1610 mg/m^3) for rats³⁵ as a basis for estimating its acute vapor toxicity toward man, perchloryl fluoride would be rated as "moderately toxic" under the classification scheme of Hodge and Sterner.⁴⁰ For comparison, acrylonitrile and hydrogen cyanide fall into the same general category, but the analogy should be carried no further. No hygienic standard for daily inhalation⁷⁶ of perchloryl fluoride has yet been established—i.e., the time-weighted average concentration (threshold limit, MAC) during a normal work day to which workers may be repeatedly exposed.³

Elkins,²⁹ in reviewing the criteria to be used in setting MAC values, recommends that, when the only data available are from animal experiments, the MAC should not exceed one-fifth the lowest concentration found to affect animals seriously on continued exposure. Since, as noted above, repeated exposure of animals for 3 months to as little as 40 ppm perchloryl fluoride has produced histopathological changes,⁶⁸ an MAC of one-fifth this concentration might very well be too high. The picture is further complicated by the demonstration of increased fluoride in the blood of exposed rodents.³⁵ If the MAC for perchloryl fluoride were to be based upon its fluorine content and the corresponding ACGIH threshold limit³ for fluoride of 2.5 mg/m^3 , then the value should not exceed 3 ppm (13 mg/m^3) perchloryl fluoride.

It is thus evident that those handling perchloryl fluoride should be adequately protected against inhalation, skin contact and ingestion. Since perchloryl fluoride is said to have a mild, sweetish odor detectable at about 10 ppm in air,⁶⁷ this may be used to warn of exposure although the development of nasal fatigue should not be overlooked.⁶⁵ No analytical methods have yet been developed specifically for the determination of small amounts (parts per million) of perchloryl fluoride in air. Although this compound is unusually stable to aqueous hydrolysis, the rapid hydrolysis in alcoholic potassium hydroxide might be used as the basis for a modification of one of the existing procedures for the determination of fluoride in air.^{23, 30, 88, 93}

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11. SAFETY CONSIDERATIONS IN HANDLING PERCHLORATES

As a general rule, perchloric acid and the perchlorates must be considered to be hazardous substances, and they should be handled with due respect for the damage to persons and property which may result from misuse or carelessness. However, the extensive and growing uses for these extraordinary chemicals suggest that the very properties which make them so valuable become the source of accidents only when the appropriate precautions are not taken. The information and recommendations presented in this chapter are not intended to provide recipes to be followed rigidly by the prospective user of perchloric acid or perchlorates, but rather to form the basis for a careful evaluation of the potential hazards involved in any proposed operating procedure.

PERCHLORIC ACID

Perchloric acid literally burst into international attention on February 20, 1947, when a violent explosion in Los Angeles, California, at the O'Connor Electro-Plating Corporation resulted in the death of 17 persons and wrecked 116 buildings with damages estimated at \$2,000,000. Newspaper accounts of the accident described grim military patrols of the devastated area and even hinted that fissionable materials (a mushroom-shaped cloud was released) were to blame for the reportedly 1,000 injured and 64 dead. A calmer appraisal of the evidence by a coroner's jury⁵⁷ and by the U. S. Bureau of Mines⁹ revealed that the explosion was caused by a mixture for the electropolishing of aluminum, consisting of approximately 150 gallons of 68 to 72 per cent perchloric acid and 70 gallons of acetic anhydride into which a plastic holder had been introduced. Furthermore, the refrigeration system for the stainless steel tank (phenolic resin-coated) had been shut off. As will be shown, it would have been rather surprising if an explosion had not taken place.

The great usefulness of perchloric acid, a virtually irreplaceable reagent in analytical chemistry, should not obscure the fact that it is a hazardous substance. But perchloric acid, like many other hazardous materials, can be used safely in a variety of ways and in quantities ranging from milligrams to hundreds of pounds, provided that its properties are understood and its hazardous character is recognized.

The physical and chemical properties of anhydrous and aqueous perchloric acid have been described in Chapter 2. The highly corrosive action

of perchloric acid upon the skin, eyes and mucous membranes has already been discussed in Chapter 10, and this hazard will not be further elaborated.

Prior to the unfortunate Los Angeles accident of 1947, a number of descriptions of explosions involving perchloric acid had appeared in the literature. In 1862, Roscoe⁸⁶ observed that a single drop of anhydrous perchloric acid falling upon charcoal, paper, wood, ether, or alcohol caused a violent explosion. He also noted explosion of the anhydrous acid on distillation, or even on storage at room temperature in the dark within 2 weeks. The fused monohydrate induced immediate combustion of wood or paper. Berthelot⁷ similarly called attention to the great heat of hydration of perchloric acid, and the explosive decomposition of both the anhydrous acid and the monohydrate. Additional warnings of the explosive reaction of perchloric acid with oxidizable substances were given by Berthelot⁷ and by Michael and Conn.⁷²

However, as late as 1936, Deiss,²¹ in giving precautionary rules for the use of perchloric acid in analytical work, complained that little attention had been given to the danger of explosion in working with perchloric acid, and cited only one reference thereto; Hackl³⁴ was able to give several more. Explosion of the heated ethanolic filtrate in the determination of potassium as the perchlorate was attributed by Deiss²¹ to the formation of the unstable ester, ethyl perchlorate, but Meyer and Spormann⁷⁰ claimed this was due to decomposition of the acid in contact with oxidizable material.

Kahane,^{53, 54} having studied some dozen explosions in the course of several thousand oxidations of organic and biological substances, recommended: (1) preliminary attack by nitric acid on the more readily oxidizable portion of the sample; then (2) dilution in an inert medium such as a large excess of aqueous perchloric acid, or a moderate amount of sulfuric acid. Balks and Wehrmann,⁵ on the other hand, while approving of the use of perchloric acid following nitric acid for the decomposition of plant samples, warned against its use on animal substances because of an explosion they had experienced with a sample of fish.

The explosive reaction of bismuth, alone or in certain alloys, with perchloric acid was attributed by Fichter and Jenny²⁷ to chloric acid or chlorine dioxide. Nicholson and Reedy,⁷⁷ however, found no evidence for the presence of the latter two compounds; nor was the explosive material bismuth perchlorate, a sample of which was found to be stable at ordinary temperatures and only slowly decomposed upon ignition. The explosiveness seemed to be inherent in the dark coating which formed on the metal, but attempts to isolate the unstable product were unsuccessful. The danger of attempting to use electrolytes to polish bismuth or bismuth alloys was emphasized by Merchant⁶⁸ who had failed to find any references on this matter in the literature on electrolytic polishing.

Dietz²³ found that explosions, which may occur when 72 per cent perchloric acid is used for the determination of chromium in steel, are apparently due to the formation of mixtures of perchloric acid vapor and hydrogen. These vapor mixtures can be exploded by the catalytic action of steel particles. The presence of steel turnings lowered the explosion temperature of such mixtures from 400 to 215°C; addition of a little water to keep the boiling temperature at 150 to 160°C (about 60 per cent acid) prevented the formation of explosive gas mixtures. Aqueous (72 per cent) perchloric acid alone was quite harmless in the absence of combustible substances.

Further reports of the care required in handling perchloric acid were published by Deiss²² and Meyer,⁶⁹ while Gabiersch²⁹ described the wrecking of a laboratory when woodwork saturated with perchloric acid was accidentally ignited. Nevertheless, Reedy,⁸³ in urging the more general use of perchloric acid as an analytical reagent, dismissed its reputation as a "treacherous explosive," and stated only that the concentrated acid is quite stable, is not exploded by shock or otherwise, and that it "is a dehydrating agent and chars wood and other cellulosic materials by the extraction of water. Very naturally, the intensity of this effect varies with temperature."

The accident at the O'Connor plant at least had the salutary effect of stimulating a reappraisal of the probable causes of perchloric acid fires and explosions and means for their prevention. Smith⁹¹ has pointed out that the hazards associated with the use of perchloric acid "are the result of lack of familiarity with its multiple properties."

Harris³⁶ examined the reports of 11 fires and explosions involving perchloric acid which occurred between 1936 and 1948 and concluded that they were caused in the following ways:

1. The digestion of samples with the acid in laboratory fume hoods used for general purpose work in which deposits of organic material were allowed to accumulate.
2. Spillage on porous material, such as sawdust and rags, which later ignited and/or exploded.
3. The contact of hot, concentrated perchloric acid with organic material, the alcohols and cellulose being particularly dangerous.
4. The mixing of perchloric acid solution and strong dehydrating agents (acetic anhydride, sulfuric acid).

The precautions suggested by Harris³⁶ for the safe handling of perchloric acid in laboratory and larger quantities are substantially the same as the current recommendations of the Factory Mutual Engineering Division which will be discussed later in this section.

Other reviews of accidents due to improper handling of perchloric acid

are those of Hikita and Asaba⁴¹ and of Moureu and Munsch.⁷⁴ Summaries of the properties of perchloric acid and recommendations for its safe use have also been published by Burton and Prail,¹¹ Marusch,⁶⁵ and Sobers.⁹⁵

There appears to be general agreement with the conclusions reached by Harris as to the causes for fires and explosions involving perchloric acid. Restated, they are: (1) the instability of pure anhydrous and aqueous perchloric acid under various conditions; (2) the dehydration of aqueous perchloric acid; and (3) the reaction of perchloric acid with other substances to form unstable materials.

Stability of Perchloric Acid

It is essential to distinguish clearly between anhydrous perchloric acid and the 70 to 72 per cent or more dilute aqueous solutions of the acid which are generally available. The aqueous solutions can be concentrated at atmospheric pressure to the azeotropic solution, boiling at 203°C/760 mm and containing 72.4 weight per cent perchloric acid. Distillation of the azeotropic solution at atmospheric pressure is accompanied by some decomposition to chlorine, chlorine oxides and oxygen. At reduced pressure (2 to 7 mm Hg), the solution can be further concentrated to the composition of the dihydrate, $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$, which contains 73.6 per cent acid (melting point, -17.8°C). The properties of the other postulated hydrates are described in Chapter 2. The monohydrate (melting point 49.9°C ⁹³), which can be prepared by dilution of the anhydrous acid with water or the dihydrate, has been stored for years in sealed capsules without discoloration or decomposition⁹²; it is, however, highly reactive and, as previously noted, spontaneously ignites wood or paper.⁸⁶

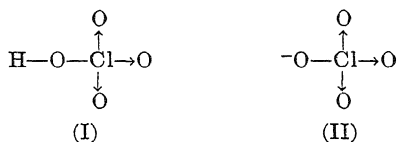
Anhydrous perchloric acid may be prepared in good yield (75 per cent) by dehydration of the aqueous acid with fuming sulfuric acid followed by distillation at reduced pressure.⁹² The anhydrous acid decomposes, sometimes explosively,⁸⁶ on boiling at atmospheric pressure, but it can be distilled without decomposition at 16°C at 18 mm.¹⁰¹ The extrapolated boiling point at 760 mm is 130°C ¹⁰¹; the melting point is -112°C .^{92, 101}

The successful distillation of anhydrous perchloric acid from mixtures with sulfuric acid at atmospheric pressure has been attributed by Zinov'ev¹⁰⁹ to the occurrence of an induction period. That is, distillation can be accomplished at temperatures above the decomposition point provided the distillation time is less than the induction period. Reliance on an induction period of unknown duration, however, can hardly be recommended as a means for reducing the hazard of the explosive, thermal decomposition of perchloric acid.

On storage, even in the dark, the anhydrous acid gradually becomes colored due to the formation of decomposition products; in this condition it may explode spontaneously. According to Missan and Sukhotin,⁷³ 97 per

cent perchloric acid decomposes, even at room temperature, with the formation of oxygen, chlorine dioxide, and chlorine trioxide; addition of 1 per cent chloral hydrate as stabilizer prevented the formation of the chlorine oxides. Smith⁹² states that anhydrous perchloric acid may be stored without explosive decomposition for 30 to 60 days at liquid-air temperatures and without coloration from decomposition products. Pure samples do not explode at ordinary temperatures for approximately 30 days,⁹² although slightly contaminated material may explode sooner.⁸⁶ If the anhydrous acid must be prepared but cannot be used within a short time, Smith⁹² recommends that it be stored as the crystalline monohydrate by addition of the calculated weight of 72 per cent acid. However, stored anhydrous acid which has become colored amber or darker should be immediately diluted with water and discarded. It cannot be emphasized too strongly that anhydrous perchloric acid must not be allowed to come into contact with organic substances such as alcohols, wood, paper, rubber, plastics, cotton, cork, etc.

The instability of anhydrous perchloric acid may be related to its occurrence in the asymmetrical, covalent form (I), in contrast to the aqueous (77 per cent) acid which is completely in the ionic form (II)^{88, 89}:



When water is added to anhydrous perchloric acid, Laman lines corresponding to ClO_4^- (II) first appear at 97 per cent acid, but the HClO_4 (I) lines continue down to about 77 per cent acid. Since the monohydrate, $\text{H}_3\text{O} \cdot \text{ClO}_4$, corresponds to 85 per cent acid, fused oxonium perchlorate must contain some of the covalent form.

Although, as noted above, some decomposition of the azeotropic solution containing 72.4 per cent perchloric acid occurs on distillation at atmospheric pressure, aqueous perchloric acid solutions are remarkably stable to heat and shock. Aqueous solutions containing less than about 75 per cent perchloric acid may be stored without change indefinitely at ordinary temperatures. Solutions of up to 60 per cent acid, exposed in closed test tubes to sunlight for several weeks, were found to be visually unchanged.²⁵ At ordinary temperatures, the aqueous acid is virtually nonoxidizing; the properties are primarily those of a strong acid, exhibiting the reactions of the hydrogen ion. The hot, concentrated acid, however, acts as a strong oxidizing agent and reduction of the perchlorate ion occurs. The point at which these two properties begin to overlap differs with the system involved.¹¹

Dietz²³ failed to obtain an explosion when 60 per cent technical per-

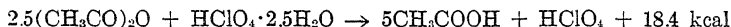
chloric acid was distilled from a flask and the residue heated to the softening point of the glass. Similarly, introduction of an electrical arc into boiling perchloric acid solution resulted only in weak, local deflagrations (*Verpuffungen*). Nor could boiling 72 per cent perchloric acid be detonated when primed with mercury fulminate or lead azide. Dietz concluded that the 72 per cent acid is harmless in the absence of combustible substances. In a similar investigation Elliott and Brown²⁵ were unable to ignite or detonate 60 per cent perchloric acid by exposure to an electric spark; also, a sample of 60 per cent acid, frozen into a steel cylinder and confined by a steel plunger, failed to ignite under the impact of a 5-kg weight dropped 300 cm.

The statement of Moureu and Munseh⁷⁴ that the 62 per cent acid may detonate under the influence of an initiating detonation probably refers to mixtures of the acid with acetic anhydride, as described later in this section.

Dehydration of Aqueous Perchloric Acid

Mixtures of perchloric acid with acetic anhydride have been used extensively for some time for the electropolishing of metals.⁵⁰ Merchant⁶⁸ warned of the explosive potential of such mixtures, and, in fact, a number of explosions (including that at the O'Connor plant) have occurred.^{51, 57, 66, 67}

Calorimetric measurements⁵⁵ of the heat of mixing aqueous perchloric acid with acetic anhydride in glacial acetic acid (20.6 ± 1.8 kcal/mole) gave results corresponding to the difference between the heats of hydration of acetic anhydride (34.8 kcal/mole) and of 69 per cent perchloric acid (16.4 kcal/mole). This can be explained on the basis of the dehydration of the perchloric acid by the acetic anhydride to form a solution of anhydrous perchloric acid in acetic acid:



The most explosive mixture would be that in which complete combustion occurs:



The energy released as a result of such a combustion (1250 kJoules/kg) falls between the values obtained from nitrocellulose and nitroglycerine. The temperature of the explosion would be approximately 2500°C, and the detonation velocity might reach 5000 to 7000 meters/sec.^{57, 66, 67} Burton and Prail¹¹ have pointed out that equimolar quantities of perchloric and acetic acids thus would, almost instantaneously, give rise to 5 moles of gas, or 112 liters at S.T.P. Assuming the ideal gas laws hold, then the gas volume

would be 1137 liters at 2500°C; that is, 1 g of the mixture would form about 7 liters of gas.

Perchloric Acid–Acetic Anhydride–Acetic Acid Mixtures

Jacquet and his co-workers^{57, 66, 67} have examined in great detail the hazardous properties of various mixtures of perchloric acid, acetic anhydride and acetic acid which are widely used in electropolishing baths. The chemistry of these mixtures and their use in acetylation have been reviewed by Burton and Praill.¹¹

Using 100 per cent acetic anhydride and 62.7 per cent perchloric acid (density 1.590 at room temperature), Jacquet *et al.* were able to demonstrate the following:

1. Although more heat is evolved when perchloric acid is added to acetic anhydride than when the addition is in the reverse order, no explosion was obtained by either order of addition when the acid and anhydride were mixed as rapidly as possible, even with the composition corresponding to complete combustion. The most serious hazard here appeared to be the possibility of spattering the operator with hot acid; addition of the acid to the anhydride was suggested as the less dangerous procedure.

2. The mixture corresponding to complete combustion (equimolar proportions of perchloric acid and acetic acid, or 68 parts by volume perchloric acid of density 1.59 to 32 parts acetic anhydride) was the most sensitive to priming; it was detonated by 0.6 g mercury fulminate. Sensitivity to priming decreased with increasing content of acetic anhydride; mixtures containing less than about 57 per cent by volume perchloric acid could not be detonated. In fact, the mixture with sufficient anhydride to take up all of the water (24.3 parts by volume perchloric acid of density 1.59 to 75.7 parts acetic anhydride) could not be detonated with 50 g pentaerythritoltetranitrate. Addition of water also reduced the sensitivity; when the amount of water corresponded to perchloric acid of density 1.50, the mixture could not be detonated even when the proportion of acid to anhydride was that required for complete combustion.

3. In testing the sensitivity to shock of the complete combustion mixture, a drop of the liquid (about 34 mg) in a metal capsule could be exploded 50 times out of 100 trials by a 1-kg weight falling 1.40 meters. Since there remained a liquid residue, the shock appeared to have initiated a local decomposition which was not transmitted throughout the liquid. When a 30-kg weight was allowed to fall through 3.5 meters onto a 5-ml flask of the mixture, there were no fumes nor could the noise of the explosion be heard.

4. A wire, electrically heated to red heat, ignited the vapors from heated mixtures containing more than 60 per cent acetic anhydride, but there were

no explosions when the wire was immersed in either the vapor or the liquid. When heated mixtures were subjected to a flame, those richest in acetic anhydride ignited at the boiling point, but with increasing perchloric acid content ignition became more difficult; the complete combustion mixture did not burn. These results suggested to the authors that a short circuit in the liquid or vapor of an electropolishing cell might ignite the bath but ought not cause an explosion, although burning of a large enough quantity might end in an explosion.

5. Solutions containing 37 per cent and 5.3 per cent (by volume) perchloric acid, respectively, and contaminated with both iron and aluminum, could not be exploded by priming with mercury fulminate.

6. A polishing solution heated to 60°C ignited when fine wood shavings were added. (The combined circumstances of local overheating from a short circuit plus organic contamination could, therefore, result in explosion.)

These important results have been summarized by Jacquet⁵¹ in the triangular diagram reproduced in Figure 11.1. Here, the apexes correspond respectively to 100 per cent perchloric acid, acetic anhydride, and water (brought in with the perchloric acid and not considering any dehydration by the acetic anhydride). Mixtures susceptible to detonation are located

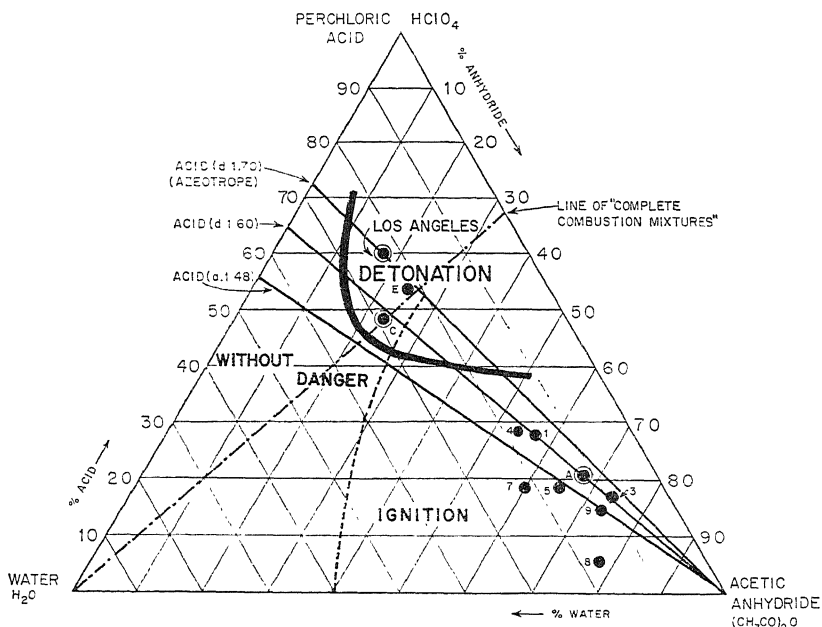


Figure 11.1. Properties of perchloric acid-acetic anhydride-acetic acid mixtures.⁵¹

in the area bounded by the arc of the curve. The mixture for complete combustion (66 volumes of 72 per cent perchloric acid and 34 volumes of acetic anhydride), which is represented by point *C*, as well as the mixture involved in the O'Connor plant accident in Los Angeles (75 volumes of 72 per cent acid and 25 volumes of anhydride) are included in this region. It will be noted that point *E*, corresponding to a mixture found to explode in laboratory tests at 60°C in the presence of cellulose acetobutyrate,^{9, 57} has the composition required for complete combustion. In the ignition zone, but outside the region of detonation, fall the mixtures (numbered points) corresponding to the compositions of the usual electropolishing baths,^{51, 68} as well as the one (point *A*) in which all of the water introduced by perchloric acid of density 1.60 is taken up by the acetic anhydride.

Mixtures of Perchloric Acid with Other Substances

As already pointed out, contamination of perchloric acid with other substances may result in ignition or explosion of the mixture. Anhydrous perchloric acid is particularly susceptible to this hazard, in addition to its capability for explosive decomposition even in the pure state.^{7, 86, 92} Aqueous perchloric acid may also cause fires or explosions under the appropriate circumstances, as described by Harris.³⁶

Some caution must be exercised in the use of perchloric acid with metals; for example, there have been cited the explosiveness of perchloric acid with bismuth^{27, 68, 77} and the catalytic action of steel particles in reducing the explosion temperature of mixtures of perchloric acid vapor and hydrogen.²³ The major cause of accidents, however, appears to be from contact of perchloric acid with organic materials, whether by formation of unstable organic perchlorates such as ethyl perchlorate,²¹ or by decomposition of the acid in contact with oxidizable substances.^{36, 69} A more useful application of this property is described in a patent²⁸ which claims a method for producing explosions on surfaces by detonating mixtures of 68 to 72 per cent perchloric acid with glycols, glycol ethers, ketones, and alcohols.

Various metal and organic perchlorates, *per se*, will be considered later in this chapter; here, we shall be concerned primarily with the reaction of perchloric acid with organic substances which may be considered to be contaminants because their presence is largely fortuitous.

In an effort to obtain quantitative data on the explosion hazards of mixtures of perchloric acid with organic materials, Elliott and Brown²⁵ conducted an extensive series of experiments to determine their sensitivity to initiation by heat, impact, sparks, flame and explosive impulses. This work has also been summarized by Lewis.⁵⁸

In the investigation of Elliott and Brown, aqueous perchloric acid was mixed with a number of organic substances typical of those with which the

acid might accidentally come in contact. For the most part, just enough perchloric acid was used to oxidize completely the other ingredients of the mixture. The composition of the various mixtures is shown in Table 11.1.

The results of slow heating tests are given in Table 11.2. For this series, approximately 0.3 cc of sample in a small, glass tube and inserted into a hole in a steel block, was heated on an electric hot plate starting at 40°C and rising to a maximum of 200°C; the time and temperature of ignition (including detonations) were noted. Elliott and Brown concluded that the concentration of perchloric acid used did not have a very great effect on the ignition temperature, and that mixtures with 40 per cent acid ignite as readily as those with 60 per cent acid. No ignitions were obtained with mixtures of perchloric acid and sulfur, or with those containing coal and 40 or 60 per cent acid. In general, addition of iron pellets to the mixture decreased the ignition temperature; this was most marked in the coal sample with 60 per cent acid which did not ignite at 200°C in the absence of iron but which ignited at 90°C with 0.4 g iron. The effect of added iron was greatest at the highest acid concentration, although there was no significant difference attributable to the amount of iron. Addition of zinc filings, active nickel catalyst, or ferric hydroxide to mixtures of perchloric acid with wood meal, coal dust or high-volatile pitch had no significant effect upon the ignition temperature.

Similar samples of perchloric acid and oxidizable material were heated rapidly and with better heat transfer by inserting the test tube into a hole

TABLE 11.1. COMPOSITION OF MIXTURES OF PERCHLORIC ACID WITH VARIOUS MATERIALS²⁵

Material	Weight Perchloric Acid/Gram Material (g)	
	100% Acid	60% Acid
Coal dust	5.0 ^a	8.3 ^a
Cotton	2.11	3.52
Excelsior	2.58	4.30
Lampblack	4.71	7.85
Linoleum	3.0 ^a	5.0 ^a
Oil (SAE 10) in kieselguhr	6.13	10.2
Paper	2.20	3.67
Pitch, high-volatile	4.5 ^a	7.5 ^a
Pitch, low-volatile	5.00	8.33
Rubber	6.10	10.2
Sugar	2.00	3.33
Sulfur	1.78	2.97
Turpentine in kieselguhr	5.85	9.75
Wood meal	2.58	4.30

^a Estimated.

in a steel plate maintained at 170°C by an oil bath. Ignition temperatures obtained by this method agreed with those of the slow heating tests described above. An important difference was that most of the rapidly heated samples detonated rather than deflagrated, while in the slow heating experiments the converse was true. Addition of red lead (Pb_3O_4) to several samples had no effect on the ignition temperature.

The burning behavior of mixtures of organic substances with 60 per cent perchloric acid was studied in two ways, unconfined and confined. In the unconfined burning experiments, no detonation was obtained with excelsior soaked with perchloric acid and ignited, nor with stoichiometric mixtures of the 60 per cent acid and wood meal on steel, lead and tin surfaces. In the confined burning experiments, 50-g charges of the same mixtures of perchloric acid and wood meal as above were enclosed in lead foil cartridges, confined in a small cannon, and ignited by a "Nichrome" coil heated to incandescence in the charge. When the mouth of the borehole was open, the charge burned completely in 1 min, accompanied by crackling and the evolution of dense acidic gases. When the borehole was closed by metal diaphragms of various bursting strengths, substantially complete, low-order detonations were obtained at 500 psi after 20 sec of burning. With stronger diaphragms, completely propagated, high-order detonations were obtained after 5 sec of burning.

One-half g samples, exposed to an electric spark on a ceramic plate, burned completely in 10 to 60 sec, but no detonations were obtained with mixtures containing 40 or 60 per cent perchloric acid.

Using mixtures of perchloric acid with the same oxidizing substances (except pitch) as shown in Table 11.2, Elliott and Brown also examined their impact sensitivity when confined between microscope cover glasses. Mixtures of either sugar or lubricating oil with 60 per cent acid were sensitive to the impact of a 17-kg weight dropped 300 cm, but no other mixtures containing 40 or 60 per cent acid could be initiated in this way. Mixtures of 70 per cent acid with coal dust, excelsior, oil, paper, sulfur, and wood meal could be initiated by a 5-kg weight dropped 50 to 300 cm. Raw cotton mixed with 70 per cent acid was less sensitive (17-kg weight dropped 300 cm detonated samples 5 times in 5 trials), but lampblack could not be initiated (maximum impact 17 kg/300 cm). When excelsior with 40 per cent acid was heated 6 hr at 130°F, the mixture could always be detonated by the 17-kg weight dropped 200 cm; further heating, however, decreased the impact sensitivity.

In comparison with mixtures of perchloric acid with oxidizable substances, the ignition temperatures (°C) and impact sensitivities (maximum fall for no detonation), respectively, of some common explosives are as follows: mercury fulminate 260°, 2 kg/4 cm; TNT 365°, 5 kg/70 cm;

TABLE 11.2. IGNITION TEMPERATURES OF MIXTURES OF AQUEOUS PERCHLORIC ACID WITH VARIOUS SUBSTANCES^{a, c}

Material	HClO ₄ Conc. (%) ^d	No Iron			0.2 g Iron			0.4 g Iron		
		Ignition Temp. (°C)	Time (min)	Remarks ^b	Ignition Temp. (°C)	Time (min)	Re- marks ^b	Ignition Temp. (°C)	Time (min)	Remarks ^b
Coal dust	40	(200)	56.5	N	(200)	56	N	(200)	56	N
	60	(195)	65	N	108.5	7.5	I	89.5	4.5	I
	70	188	43	I	(200)	65	N	200	65	I
Cotton	40	170.5	25.5	L,H	144	14.5	I	151.5	17	I
	60	170	31	I	124	9.5	I	119.5	8.5	I
	70	(198)	50	N	132.5	11.5	I	130	11	I
Excelsior	40	171	26.5	H	151	17	I	146	18	I
	60	188	60	N	130.5	10	I	122.5	8.5	I
	70	164	24	N,I,L	117	9	I	121.5	10.5	I
Lampblack	40	176.5	37.5	I	(190)	50	N	(190)	50	N
	60	—	—	—	171	27	I	—	—	—
	70	(195)	60	N	170	26	L	171	26.5	D,L
Linoleum	40	167	23	I,L	173.5	28.5	I	181.5	35	I
	60	165.5	42	I,H	(200)	65	N	(200)	65	N
	70	118	8	L	118.5	7	D,L	124.5	8.5	D
Oil (SAE10) in kiesel- guhr	40	(190)	45	N	(190)	45	N	(190)	45	N
	60	165	33	D	147.5	16	?,I	133	12	I
	70	(180)	50	N	137.5	13.5	I	137.5	13.5	I
Paper	40	157	20.5	I	149.5	17	I,D	151.5	18	D,L
	60	173	30	I	127	10	I	127.5	10.5	I
	70	(196)	60	N	118.5	9	I	125	10	I
Pitch, high- volatile	40	176	39.5	I,L	(189)	62	N	(190)	57	N
	60	118.5	7.5	I,H	—	—	—	88.5	4	I
	70	(200)	67	N	(200)	67	N	(200)	65	N
Pitch, low- volatile	40	(190)	57	N	(190)	57	N	(198)	80	N
	70	180	40	I	(200)	67	N	(200)	67	N
Rubber	40	171	23	I	(198)	80	N	(198)	80	N
	60	170	42	I	(200)	65	N	(200)	65	N
	70	161.5	19	I	(196)	60	N	(196)	60	N

^a Average values have been calculated from the ignition temperatures for the 2-5 replicate determinations reported by Elliott and Brown²⁸ in which ignition occurred, except as noted under c, below.

^b N = no ignition; I = ignition; D = detonation; L = low-order detonation; H = high order detonation. Use of more than one symbol indicates variable results in replicate determinations.

^c Value in parentheses indicates no ignition up to this temperature. For replicate determinations, the highest test temperature reached and the corresponding time are given.

^d Concentration in water solution.

TABLE 11.2 (Continued)

Material	HClO ₄ Conc. (%) ^d	No Iron			0.2 g Iron			0.4 g Iron		
		Ignition Temp. (°C)	Time (min)	Remarks ^b	Ignition Temp. (°C)	Time (min)	Re- marks ^b	Ignition Temp. (°C)	Time (min)	Remarks ^b
Sugar	40	—	—	—	154.5	21.5	I	154.5	21.5	I
	60	175.5	31	I,D,H	126	10.5	I,D	115.5	8.5	I
	70	174.5	31	I,H	115.5	9.5	I,D	125	12	H
Sulfur	40	(200)	57	N	145	15	I?	(200)	57	N
	60	(195)	65	N	(166)	19	N	143	13	—
	70	(190)	58	N	(190)	58	N	(190)	58	N,I
Turpentine in kiesel- guhr	40	(195)	65	N	(195)	65	N	(195)	65	N
	60	160	28	I	136.5	13	I	141.5	12.5	I
	70	149.5	18	I	135	13.5	I	132.5	12.5	I
Wood meal	40	171	27	D,H	161	23	L	162	22.5	D, L
	60	169	29.5	I,D,H	136	14	D,H	122	9	D, L, H
	70	155	19.5	D,L	108.5	8	H	122	10.5	H

black powder 370°, 2 kg/100 cm; 40 per cent nitroglycerin dynamite 275°, 24 kg/25 cm; picric acid 360°, 2 kg/30 cm.

No ignitions were obtained with the U. S. Bureau of Mines friction pendulum apparatus (iron shoe) on mixtures of 70 per cent perchloric acid with excelsior, paper, wood meal, and paper with 50 per cent glass.

Attempts to detonate mixtures containing 50 and 40 per cent acid by initiation in glass bottles with a No. 8 detonator were unsuccessful, but 60 per cent perchloric acid with wood meal detonated with the same order of violence as TNT. A better comparison with the explosive strength of TNT was obtained in a large ballistic mortar, using No. 6 detonators to initiate charges consisting of mixtures of 60 per cent acid with wood meal or cotton (100-g charge, 800-g fire-clay stemming). The swing of the cannon (cm) in these tests was as follows:

TNT	25.6
cotton	24.4
wood meal	
stoichiometric mixture	27.0
90% theoretical O ₂	26.8
80% theoretical O ₂	25.7
50% theoretical O ₂	23.5

Mixtures with lampblack and carbon could not be initiated by a No. 6 detonator. The rate of detonation of a mixture of 60 per cent perchloric acid and wood meal was found to be 3,000 m/sec. Since the mixture was com-

pressed only slightly in the tube, it was believed that a higher loading density would have resulted in a considerably greater rate of detonation. This would be consistent with the explosion rate of 5,000 to 7,000 m/sec estimated for the stoichiometric mixture of perchloric acid and acetic acid.⁵¹

Stoichiometric mixtures of 10, 40, and 60 per cent perchloric acid with wood meal or excelsior, exposed in closed glass tubes to sunlight for 29 days, showed no visual evidence of extensive chemical reaction or decomposition. Exposure to sunlight also appeared to have little effect on the ignition temperature of samples subsequently subjected to the slow heating test described above.

Safe Handling of Perchloric Acid

Because of the hazard from spontaneous, explosive decomposition on storage and from violent reaction with traces of contaminants, it seems to be generally agreed that anhydrous perchloric acid should be prepared only when absolutely necessary for research purposes, and then only in very small quantities with appropriate precautions. The anhydrous acid should be kept at the lowest temperature available for a minimum time, and must not be allowed to contact any oxidizable substances. Distillation, if required, should be conducted at reduced pressure (16°C/18 mm).

Local ordinances should be consulted prior to any preparation of anhydrous perchloric acid, since special permits may be required by various regulatory agencies. The U. S. Interstate Commerce Commission¹³ prohibits the shipment of perchloric acid in excess of 72 per cent concentration, and most states use the ICC regulations in controlling the intrastate shipment of hazardous materials. California¹² requires that, except for small quantities in laboratories (1 lb), the methods and process proposed for the use of perchloric acid or its hydrates must be submitted for approval to the Division of Industrial Safety. The "Dangerous Chemicals Code" of the City of Los Angeles⁵⁹ specifically prohibits the formation of anhydrous perchloric acid "under any circumstances," limits concentrates in excess of 72 per cent by weight to chemical laboratories "for purposes of investigation and instruction," and requires approval of the Fire Department for any proposed use of perchloric acid or its hydrates except for small quantities in laboratories. A new version of the Los Angeles Fire Code will be published in 1960.

There is no question that aqueous perchloric acid, of 72 per cent or less concentration, is an essential analytical reagent, and that it has been used safely in countless thousands of analyses. Nevertheless, the occasional occurrence of accidents points to the need for frequent repetition of the simple but necessary safety requirements. Following are the recommendations of the Committee on Use of Perchloric Acid in Methods of Analysis of the Association of Official Agricultural Chemists⁴⁹:

Perchloric acid.—Contact of HClO_4 solution with oxidizable or combustible materials or with dehydrating or reducing agents may result in fire or explosion. Persons using this acid should be thoroughly familiar with its hazards, and safety practices should include the following precautions:

a. Remove spilled HClO_4 by immediate and thorough washing with large quantities of water.

b. Hoods and ducts for HClO_4 vapor should be made of chemically inert materials and so designed that they can be thoroughly washed with water. The exhaust system should discharge in a safe location, and the fan should be accessible for cleaning.

c. Avoid the use of organic chemicals in hoods employed for HClO_4 digestions.

d. Use goggles, barrier shields, and other devices as may be necessary for personnel protection.

e. In wet combustions with HClO_4 treat the sample first with HNO_3 to destroy easily oxidizable organic matter.

f. Contact of HClO_4 solution with strong dehydrating agents such as P_2O_5 or concentrated H_2SO_4 may result in formation of explosive anhydrous HClO_4 . Exercise special care in performing analyses requiring the use of HClO_4 with such agents.

g. *See also:* (1) "Perchloric Acid Solution," Chemical Safety Data Sheet SD-11 (1947), Manufacturing Chemists Association, 1825 Connecticut Ave., N.W., Washington 9, D.C.; (2) "Applied Inorganic Analysis," W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, 2nd Ed. 1953, pp. 39-40, John Wiley & Sons, Inc., New York; (3) "Notes on Perchloric Acid and Its Handling in Analytical Work," *Analyst*, **84**, 214-216 (1959).

The construction of fume hoods for perchloric acid service has been described by Sobers⁹⁵ and by Smith.⁹⁴ The concise recommendations of the Factory Mutual Engineering Division²⁶ regarding perchloric acid hoods (preferably reserved for perchloric acid service only) are as follows:

Fume hoods should be noncombustible, constructed of metal or stoneware, and left unpainted or protected with an inorganic coating such as porcelain. A water spray is desirable for washing down the hood after perchloric acid fuming. Otherwise, a separate hood should be reserved for perchloric acid use only. Stoneware hoods equipped with water spray for washing down are commercially available. Ducts must not be manifolded and should take the shortest path to outdoors. Use an electric hot plate or heating jacket, a steam bath, or an electrically or steam-heated sand bath for heating reaction vessels. Do not use gas flames or oil baths for heating. Provide a generous supply of water extinguishers.

Substantially the same recommendations for the handling, storage, and dispensing of aqueous perchloric acid have been made by Harris,³⁶ the Manufacturing Chemists' Association,⁶² the National Safety Council,⁷⁶ the Association of Casualty and Surety Companies,⁴ and the Factory Mutual Engineering Division.²⁶ Those planning to use perchloric acid should become thoroughly familiar with the properties of perchloric acid solutions and the recommendations of the agencies cited. In fact, the "Dangerous Chemicals Code" of the City of Los Angeles⁵⁹ states that compliance with the recommendations of the Manufacturing Chemists' Association "shall be considered prima facie evidence of the exercise of reasonable safety measures."

While the data sheet of the Manufacturing Chemists' Association⁶² is a little more detailed, the more recently published recommendations of the Factory Mutual Engineering Division²⁶ for handling laboratory quantities are brief but to the point (the section on fume hoods has been quoted above):

a. Confine the amount of perchloric acid in the working area to the quantity needed for current work. Several 1-lb bottles or two 7-lb bottles are the maximum amount of storage advisable in a laboratory building. A liquid ounce of perchloric acid is usually sufficient for a single analysis. Each bottle used for current work should be kept in a glass or ceramic dish large enough to hold the contents of the bottle. When spillage occurs, flush the liquid away with large quantities of water. Bottles not in active use should be isolated in noncombustible cabinets away from combustible materials and chemicals.

b. Keep perchloric acid storage, beyond immediate requirements, in a detached, isolated building, away from combustible materials. Where satisfactory arrangements cannot otherwise be made, an ordinary garbage can buried with the top projecting above the ground will provide a good storage location for small quantities. A tight wooden box inverted over the can will provide adequate protection against temperature extremes.

c. For large quantities, the storage location should be a detached building of noncombustible construction. Combustible materials and other chemicals should not be stored in the same building.

d. Store carboys preferably on a raised steel track mounted on an acid-resisting brick, concrete treated with sodium silicate, or steel floor. Provide drainage facilities and hose for diluting leakage or spills.

e. Bulk storage should be examined periodically, and acid that has become contaminated and discolored should be disposed of as follows: pour the contaminated acid into approximately 10 times its volume of cold water in a porcelain or glass vessel. Stir and pour down the acid sewer. Follow this by flushing with large quantities of water.

f. A location used for dispensing perchloric acid from large containers into smaller containers should preferably be cut off from other occupancies, and combustible material should be kept out of the area. Store minimum quantities of material to supply daily requirements. Install a drained, noncombustible floor of concrete or metal and provide water connections readily available for flushing away any acid that may be spilled.

g. Provide operators who handle perchloric acid in quantities with personal safety equipment, including gloves, sleeves, apron, and boots of rubber and eye shields or goggles for face protection.

Rather than placing unquestioning reliance on the preceding rules, it is emphatically recommended that the prospective user should first become familiar with the properties of perchloric acid, and then, for each case, give the most careful consideration to the proposed experimental conditions and operating procedure.

Perchloric acid, provided the concentration does not exceed 72 per cent by weight, is classified by the Interstate Commerce Commission¹³ for shipment as a corrosive liquid. Perchloric acid solutions, in inside bottles hav-

ing a capacity not over 1 lb or 16 oz by volume each enclosed in a metal can in the outside container are, unless otherwise provided, exempt from specification packaging, marking, and labeling requirements, except that marking the name of the contents on the outside container is required for shipments via carrier by water. Each box with larger inside containers and each carboy must bear the ICC white acid label. The maximum quantity which may be shipped in one outside container by rail express is 7 lb. By air,⁹⁰ the net quantity allowed per package is 1 lb within the United States (1 qt outside the United States) aboard passenger aircraft, or 7 lb within the United States (7 pints outside the United States) aboard cargo aircraft. Packaging requirements of the Interstate Commerce Commission¹³ are as follows:

Section 73.269—Perchloric Acid. (a) Perchloric acid in excess of 72 per cent must not be shipped. When not exceeding 72 per cent strength must be packed in specification containers as follows:

(1) Spec. 15A, 15B, 15C, 16A, or 19A. Wooden boxes with glass inside containers consisting of glass bottles over 7 pounds capacity each cushioned with incombustible mineral material in amount sufficient to absorb the acid.

(2) Spec. 1A, 1C, 1D, or 1E. Glass carboys, in boxes, kegs or plywood drums.

(3) Spec. 1X. Boxed carboys of 5 to 6 gallons capacity; single-trip for export only. For shipment by common carriers by water to noncontiguous territories or possessions of the United States and foreign countries; shipments from inland points in the United States which are consigned to such destinations are authorized to be transported to ship side by rail freight in carload lots only and by motor vehicle in truckload lots only.

(b) Cushioning for carboys must be incombustible mineral material, elastic wooden strips, natural cork blocks or rubber blocks. Other materials may be used if approved by the Bureau of Explosives. The use of hay, excelsior, loose ground cork, or similar materials, whether treated or untreated, is prohibited.

(c) Perchloric acid in any quantity must not be packed with any other article.

(d) Closures for bottles. Required as follows:

(1) Glass stoppers ground to fit and held in place by plaster of Paris covered by a strong cloth securely tied.

(2) Threaded-type acid-resistant caps with a gasket or lining impervious to the acid and sufficiently resilient, or cushioned, to give an acid-proof closure; at least one complete continuous thread is required to be engaged when bottle is closed for shipment.

(e) Inside containers must be well cushioned. All material for cushioning must be incombustible mineral material, such as whiting, mineral wool, infusorial earth (kieselguhr), asbestos, sifted ashes, or powdered china clay, etc. The use of hay, excelsior, ground cork, or similar material, either treated or untreated, is prohibited. Where the cushioning material is very fine or powdery, separate partitions for the individual inside containers should be provided to prevent the bottles from shifting and coming in contact with each other, and the box must be tight to prevent sifting of cushioning material.

(1) Cushioning of inside containers in outside wooden boxes by means of elastic packings, such as wooden strips or large corks fastened securely in position, is authorized if the completed package will pass the swing test prescribed for boxed carboys, in Spec. 1A.

U. S. Coast Guard regulations¹⁰⁰ covering dangerous articles on board vessels are similar to the ICC requirements. Stowage on cargo vessels is "on deck protected"; shipment is not permitted aboard passenger or ferry vessels.

Many states now have laws and regulations governing the precautionary labeling of hazardous chemicals, although some of these are restricted to packages intended for household use. A compilation of these requirements has been published by the Chemical Specialties Manufacturers Association.¹⁶ It also appears likely that a Federal hazardous substances labeling act will be passed in the near future, since many organizations (Manufacturing Chemists' Association, Chemical Specialties Manufacturers Association, American Conference of Governmental Industrial Hygienists, American Medical Association, etc.) have been sponsoring such action in recent sessions of the United States Congress. Since they are hazardous materials, precautionary labels should, therefore, be affixed to containers of perchloric acid solutions. The following precautionary label is recommended by the Manufacturing Chemists' Association^{62, 63} and is required in California¹²:

PERCHLORIC ACID

DANGER! STRONG OXIDANT.

**CONTACT WITH OTHER MATERIAL MAY CAUSE FIRE OR EXPLOSION,
ESPECIALLY IF HEATED.**

CAUSES SEVERE BURNS.

Keep container closed and away from heat.

Store separately from, and avoid contact with, dehydrating agents and other materials.

Do not get in eyes, on skin, on clothing.

In case of spillage, flush with plenty of water and remove contaminated articles.

In case of contact, immediately remove all contaminated clothing and flush skin or eyes with plenty of water for at least 15 minutes; for eyes, get medical attention.

Wash clothing before re-use.

It is also advisable to affix the same precautionary label to outer shipping containers of perchloric acid in addition to any label warnings required by the Interstate Commerce Commission, or applicable statutes, regulations or ordinances.

PERCHLORATES

Perchlorates have been widely used in explosive compositions since the Carlson patents were granted in 1897^{14, 15} and, more recently, in propellant mixtures (see Chapter 8); Davis²⁰ has described a number of uses of perchlorates in pyrotechnics. Yet, sufficient data do not appear to have been published to develop a definitive picture of the relation of perchlorate structure to predictable hazard. Recommendations for the safe handling

of perchlorates can, therefore, be presented only on a broad qualitative basis. It is hoped that the considerable body of information which no doubt resides in classified and proprietary documents may some day be made available to supplement this.

In general, perchlorates are hazardous in proportion to the degree of sensitivity to heat or shock exhibited by a given compound or perchlorate-containing mixture under appropriate conditions. The amount of energy required may range from as little as slight friction, warming or a bump, to a conflagration, severe impact, or initiation by a detonator. The result may be ignition or explosions of varying degrees of intensity, although, as has been shown, many applications have been made of the controlled use of these properties.

Davis²⁰ included *m*-nitrophenyldiazonium perchlorate among his examples of primary explosives or initiators, that is, those which explode or detonate when heated or subjected to shock. Ammonium perchlorate, on the other hand, was cited as an example of a high explosive, that is, one which requires the shock of the explosion of a booster charge (a composite of primary and secondary explosives) for detonation.

Both Davis²⁰ and Marshall⁶⁴ have stated that the perchlorates are more stable and less sensitive than the chlorates, and are much safer in contact with combustible substances. Cook,¹⁷ however, believes that despite the many developments described in the patent literature of chlorate and perchlorate explosives, "the great hazards connected with their manufacture and use have prevented their extensive development, at least in America." Although the latter statement is probably too facile a dismissal of perchlorates as excessively hazardous, at the least it suggests the great need for a more precise exposition of the circumstances under which any given perchlorate or perchlorate composition may be safely used. An accidental explosion (or fire) may, after all, be considered as the unexpected demonstration of an otherwise useful property.

Pletz⁸¹ subdivided all explosives into eight classes, each of which includes certain definite structural groupings ("explosophores") upon which are dependent the explosive properties of any given substance. ("Auxoploses" are groups which fortify or modify the explosive properties brought about by the explosophore.) The $-\text{OClO}_2$ and $-\text{OClO}_3$ groups, connected to inorganic or organic radicals, were included by Pletz as Class V explosophores. Lothrop and Handrick,⁶⁰ in attempting to relate the performance of pure organic explosive compounds to their constitution, introduced the term "plosophore," defined as "a group of atoms which on substitution into a hydrocarbon is capable of forming an explosive compound." (The name "auxoplosive" was given to substituent groups which alter explosive properties.) A further subdivision was made into primary and secondary plosophores.

phores, depending on the "effectiveness and consistency in producing power." The primary phosphores include the following groups: nitrate ester, aromatic nitro, aliphatic nitro, and nitramine. The secondary phosphores include such groups as: azo, nitroso, peroxide, ozonide, perchlorate, etc.

It was concluded⁶⁰ that the power of primary phosphoric compounds is directly related to oxygen balance*, and is at a maximum in compounds whose balance is close to zero. For secondary phosphores (including perchlorates), this relationship occasionally holds, but it is not consistent. Four organic perchlorates (ethyl perchlorate; ethylenediamine diperchlorate; 1,2-propylenediamine diperchlorate; 1,3-propylenediamine diperchlorate), each of which has a negative oxygen balance, exceed the power and brisance of TNT (=100) in the lead block expansion test, while ammonium perchlorate (oxygen balance positive) is considerably less powerful.

Although no attempt will be made to catalog the individual explosive properties of the many known perchlorates, a brief review will serve as a background for the safety recommendations to be given later in this section. As in the case of perchloric acid, it is important to emphasize that the prospective user of a perchlorate should give careful consideration to the potential hazards in any proposed experimental conditions and operating procedure.

Inorganic Perchlorates

The pure alkali metal and alkaline earth perchlorates are not decomposed at temperatures up to about 250 to 400°C.^{88, 91} The thermal decompositions of a number of the pure salts have been studied by Gordon and Campbell⁸²; the results are discussed in Chapters 2 and 3. Mention may also be made of the decomposition of solid potassium perchlorate by 50 kv x-rays.³⁷ The average amount of x-ray energy absorbed per ClO_4^- ion decomposed was found to be 19 ± 2 ev corresponding to 440 kcal/mole. The main products of the primary decomposition were chlorate and chloride, but small amounts of unidentified oxidizing substances were also formed. The chlorate decomposed by a secondary reaction to chloride.

Raisor⁸² found that the decomposition of ammonium perchlorate was negligible at 210°C, fairly rapid (two-step) at 220°C, and still more rapid (single-step) at 240°C. The two-step decomposition was strongly catalyzed

* Oxygen balance = $[-1600 (2x + y/2 - z)]/\text{molecular weight}$

where x = number carbon atoms, y = number hydrogen atoms, and z = number oxygen atoms.

by powdered copper metal or cupric oxide, and to a lesser extent by sodium chlorate, lithium chlorate or potassium dichromate. Ferric oxide had a negative catalytic effect on the first decomposition step and some positive effect on the second step, while boric acid was without effect.

Some observations on ammonium perchlorate made by a French explosives commission in 1907 are cited by Davis.²⁰ Pieces of cotton cloth dipped into a solution of ammonium perchlorate and dried, burned more rapidly than cloth treated with potassium chlorate but less rapidly than when impregnated with sodium chlorate. Ammonium perchlorate ignited in contact with a hot wire, and burned vigorously with the release of choking white fumes until the hot wire was removed. In a drop test, the sensitivity of this salt to shock was about the same as that of picric acid, but its sensitivity to initiation was less. A 5-kg weight dropped 50 cm caused explosions in about 50 per cent of the trials. The detonation of ammonium perchlorate gently tamped into a 16 cm x 26 mm cartridge was propagated 20 mm into the tube by a 25-g picric acid booster, and 35 mm by 75 g picric acid. The temperature of explosion of ammonium perchlorate was calculated to be 1084°C.

Confirmation of the relative insensitivity of ammonium perchlorate to heat and to initiation has been provided by Naoum and Aufschläger.⁷⁵ Quantities of up to 5 g did not explode whether heated slowly or rapidly, although Dodé²⁴ reported that explosive decomposition occurred near 400°C. In Trauzl lead block tests, dry ammonium perchlorate was detonated by a No. 6 cap, but when the salt contained 5 per cent moisture a No. 8 cap gave only a weak, partial detonation.⁷⁵ The same investigation⁷⁵ gave a rate of detonation in a 60-mm diameter iron tube of 3800 m/sec; values of about 2500 m/sec, obtained in 35 mm tubes with 110 g pressed tetryl and 25 g pressed picric acid primers, have also been recorded.¹⁰³ Smith⁹¹ stated that a No. 13 detonating cap is required to explode ammonium perchlorate.

More recently, Schumacher and Stern^{87, 97} examined the initiation sensitivity of ammonium perchlorate and obtained the following results with material packed loosely into a 4 x 1½ in. cardboard cylinder standing on a steel plate: a No. 8 cap (equivalent to 2 g mercury fulminate) appeared to have caused a partial detonation; an XC-32 detonater (equivalent to 10 g mercury fulminate) exploded ammonium perchlorate with moisture contents of 0.02 and 1.0 per cent, but not when the moisture content was 6.0 per cent. With 10 lb of ammonium perchlorate in 1-gal. cans, a No. 8 cap only ignited the contents, while detonation was initiated by an XC-32 cap; no induced detonation occurred when several such cans were separated by ⅞ in. from the one which was exploded. No explosion or ignition of relatively pure ammonium perchlorate was observed in 100 trials in a Bureau

of Mines pendulum friction apparatus (steel shoe), although some crackling or snapping was heard in one of the trials.

Stern⁹⁷ also examined the impact sensitivity of ammonium perchlorate using 0.20-g samples of oven-dried material in an apparatus similar to that described by Davis.²⁰ He found that an 11.0-lb weight dropped 86 in. produced detonations in 1 trial out of 10; with 1 and 5 per cent added iron powder, 3/10 and 6/10 detonations, respectively, were obtained (10 per cent iron caused no further change). With 1, 5, and 10 per cent added manganese dioxide, 3/10, 2/10, and 1/10 detonations, respectively, were obtained when the 11.0-lb weight was dropped 86 in., but there appeared to be a maximum increase in impact sensitivity at about 1 per cent MnO_2 since an 18.0-lb weight dropped 67 in. produced 10/10, 9/10, and 8/10 detonations with 1, 5, and 10 per cent MnO_2 , respectively. These values indicate that while pure ammonium perchlorate is considerably less impact-sensitive than other common explosives,⁸⁵ the presence of other materials, even in small amounts, may considerably enhance the sensitivity. This point will be further examined later in this chapter.

Several explosions which have been reported^{21, 65, 74} as occurring during the determination of potassium as the perchlorate are probably attributable to heating in the presence of concentrated perchloric acid and traces of alcohol. Such accidents may be prevented by avoiding heating (except on a water bath if necessary) and, particularly, evaporation to dryness. Marusch⁶⁵ states that the alcohol may be recovered from alkaline solution since the alkali perchlorates are stable above 300°C.

There have been several reports of explosions resulting from the use of magnesium perchlorate as a drying agent. Stross and Zimmerman⁹⁸ dried 11,000 samples of alkali-washed hydrocarbon gas with magnesium perchlorate during 7 years without accident. However, one sample containing butyl fluoride caused a purple discoloration of the magnesium perchlorate with subsequent explosion of the latter. The authors recommend that flammable materials, mineral acids or substances liable to hydrolyze to mineral acids should be excluded in the use of magnesium perchlorate as a drying agent. Heertjes and Houtman³⁸ experienced an explosion when anhydrous magnesium perchlorate, used in drying unsaturated hydrocarbons, was heated to 220°C. They too urge that there should be no contact with acids. Dam,¹⁸ who described an explosion of magnesium perchlorate used to dry argon, recommended that warming and contact with oxidizable substances should be avoided. Marusch⁶⁵ has pointed out that traces of perchloric acid may remain from the manufacture of magnesium perchlorate and that explosions can occur because of this free acid or the esters formed from it.

Silver perchlorate has exploded when the dry, caked salt, twice recrystallized from benzene, was gently broken up in a mortar.¹⁰ This accident was attributed to the benzene-silver perchlorate addition compound, usually considered to be stable up to 145°C. Brinkley¹⁰ also cited a similar explosion of the ethanol-silver perchlorate addition compound, and notes that, under some (unspecified) circumstances, violent decomposition of perchlorates dissolved in organic solvents may take place. Hein³⁹ similarly experienced an explosion when a silver perchlorate filter cake was being pulverized in a mortar. He found that the perchloric acid used to prepare the salt was free of chloride, chlorate and organic compounds; the silver nitrate used contained only spectroscopic traces of copper and iron; and there was no ether-silver perchlorate complex formed. It was concluded that the explosion was due to silver perchlorate alone. Sidgwick⁸⁸ suggested that all of the various complexes of silver perchlorate with organic compounds are liable to explode.

Anhydrous lead perchlorate is, like silver perchlorate, readily soluble in many organic solvents. An investigation of this property was discontinued after the violent explosion of a saturated solution of the salt in anhydrous methanol at room temperature occurred when the flask containing the solution was disturbed.¹⁰⁶

In an attempt to prepare hydrazine nickel (II) perchlorate, $\text{Ni}(\text{N}_2\text{H}_4)_2 \cdot \text{ClO}_4$, the blue precipitate formed from nickel perchlorate and hydrazine in water exploded violently when a glass stirring rod was introduced into the suspension.⁶¹ Dry hydrazine perchlorate, itself, can be detonated by shock or friction.⁶ Decomposition of the latter salt begins at 145°C and is completed at about 230°C if heating is careful; strong heating, however, induces a fairly strong deflagration. Anhydrous hydrazine perchlorate has a shock sensitivity comparable to that of initiating explosives, although the hydrate is considerably less sensitive. Using a standard impact sensitivity apparatus, a 3.5-kg weight dropped 0.5 in. detonated a carefully dried sample in 50 per cent of the trials; when the material was finely ground, a drop of only 0.25 in. detonated the sample.¹⁰⁷ The same finely powdered material could not be initiated with a Tesla coil, nor by an electric squib with a 0.015-in. "Nichrome" bridge; under the same conditions, lead styphnate detonated. With a 0.030-in. "Nichrome" bridge, the hydrazine perchlorate burned rapidly. While the dried salt was being carefully ground in a laboratory mortar, using the weight of the pestle as the only pressure applied, a detonation occurred.

Fluorine perchlorate, ClO_4F , has been found to be particularly unstable.⁸⁴ The pure compound exploded in three attempts to determine the freezing point (-167.3°C). The gas (b.p., $-15.9^\circ\text{C}/755\text{ mm}$) was readily exploded by a small flame, sparks, grease, specks of dirt, or contact with

rubber tubing; one sample exploded on contact with potassium iodide solution.

Perchloryl fluoride, FClO_3 , alone is a highly stable compound, but since it is a powerful oxidizing agent (particularly at elevated temperatures) it must be handled with care when it is in contact with oxidizable substances.^{46, 47, 80} Its properties are described in detail in Chapter 5. Papesch⁷⁹ recently reported that a mixture of the vapors of perchloryl fluoride and methyl alcohol ignited and exploded when a final portion of sodium methylate was added during the synthesis of ethyl 2,2-difluoroacetoacetate. The salts of perchlorylamide are sensitive when dry and may detonate.⁸⁰

Gordon and Spinks³³ reported that nitroxyl (or nitryl) perchlorate, $\text{NO}_2 \cdot \text{ClO}_4$, reacts readily with most organic materials. With benzene it gave a slight detonation and a flash; sharp detonations, with ignition of the liquid, occurred with acetone and ether, while there were rapid reactions without explosions with alcohol and glycerol. Later, Goddard *et al.*³¹ found that the pure material decomposed without exploding above 135°C , giving off NO_2 . They too obtained ignitions and explosions when nitroxyl perchlorate was reacted with organic compounds.

Nitrosyl perchlorate, NOClO_4 , reacts with water, evolving nitrogen oxides.⁴⁴ It ignites urea, ethanol and acetone on contact; with dry ether, gas evolution is followed by explosion. Extremely violent reactions are obtained with aromatic primary amines (aniline, *o*- and *p*-toluidine, xylidine); dry pyridine decomposes, but is not ignited.

Mixtures of inorganic perchlorates, whatever their individual stabilities may be in the pure state, must be handled with exceptional care. The Bureau of Mines,⁵² for example, found that a perchlorate mixture used in land mines (composition unspecified) detonated so severely in a standard pendulum friction test (fiber shoe) that the tests had to be discontinued. In a pressure friction test, the mixture was only slightly less sensitive than mercury fulminate. It was 10 times more sensitive than mercury fulminate to a static spark of lower energy than can be generated and discharged from the human body. Kabik⁵² also cited three industrial explosions involving a photoflash composition containing potassium perchlorate with aluminum and magnesium powders. Tests of mixtures containing potassium perchlorate with nickel, titanium, and infusorial earth resulted in such severe explosions with the fiber shoe on the pendulum friction apparatus that the weight of the test sample had to be reduced from the standard 7 g to 2 g. Even with this weight reduction, four of six mixtures tested failed the fiber shoe test. Whether confined or unconfined, all of these mixtures required less energy from a static spark to ignite them than can be dis-

charged from the human body. Davis²⁰ notes that flash cracker mixtures of potassium perchlorate with sulfur can be exploded on an iron anvil by a moderately strong blow with an iron hammer.

Elliott and Brown²⁵ examined the impact sensitivities (5-kg weight) of mixtures of a number of perchlorate salts with sulfur and with sulfur and sand. The results are summarized in Table 11.3. In general, the test mixtures were found to be of the same order of sensitivity as railway torpedoes, which are usually combinations of potassium perchlorate, sulfur, and sand; for such torpedoes, the maximum height of fall of a 5-kg weight for no detonations was 20 cm. For some other common explosives, the maximum heights of fall for no detonations (weight/distance) were: mercury fulminate, 2 kg/4 cm; TNT, 5 kg/70 cm; black powder, 2 kg/100 cm; 40 per cent nitroglycerin dynamite, 24 kg/25 cm; picric acid, 2 kg/30 cm.

In tests²⁵ with the friction pendulum apparatus (iron shoe), ignitions were always obtained with a mixture of potassium perchlorate and sulfur containing 50 per cent sand (Elliott and Brown use the term "ignition" to include detonations). Tests of a mixture of potassium perchlorate and sulfur initiated by a No. 6 detonator in a large ballistic mortar (100-g charge, 800-g fire-clay stemming) resulted in an 18.2-cm swing of the cannon. In comparison, under the same conditions the cannon swing for TNT was 25.6 cm; the swing was 27 cm for a stoichiometric mixture of 60 per cent perchloric acid and wood meal.

Organic Perchlorates

Many perchlorate salts of organic bases are known; these include substances in which the central atom has a complete outer shell of eight electrons, as in the oxonium, sulfonium and ammonium salts. Marusch⁶⁵ and Burton and Praill¹¹ have noted that, except for the diazonium salts, these compounds involve little hazard unless they are subjected to heat or shock.

Datta and Chatterjee¹⁹ published data on the "temperature of explosion" of 41 amine perchlorates dropped into test tubes preheated in a bath; the values for what Burton and Praill prefer to call the "temperature of ignition"¹¹ were in the region of about 250 to 300°C. The lowest ignition temperature observed was 215°C (hydrazine diperchlorate) and the highest was 367°C (guanidine perchlorate). The ignition temperature of 250°C for aniline perchlorate found by these authors¹⁹ is the same as that reported earlier by Spallino⁹⁶ for the explosive decomposition of this salt.

Explosions have been reported^{56, 74, 108} to have occurred during the purification of pyridine via the perchlorate by the method of Arndt and Nachtwey.² As a result of these accidents, Kuhn and Otting⁵⁶ examined the properties of pyridine perchlorate in some detail. The salt (m.p., 288°C)

TABLE 11.3. IMPACT SENSITIVITIES OF PERCHLORATE-SULFUR MIXTURES^{25a, b, c}

Perchlorate salt	Other Components of Mixture	Height of fall (cm)	Detonations (%)
ammonium	sulfur + 50% sand	15	100
		10	80
		5	40
barium	sulfur + 50% sand ^d	10	100
		7.5	40
		5	0
calcium	sulfur + 50% sand	35	80
		30	40
		25	20
lead	sulfur + 50% sand	50	100
		40	50
		30	40
lithium	sulfur + 50% sand	150	100
		50	80
		45	0
lithium	sulfur + 50% sand ^d	20	100
		20	70
		15	0
magnesium	sulfur + 50% sand	30	80
		25	20
magnesium	with 50% sand	300	20
		200	20
		100	20
magnesium ^e	with 50% sand	300	20
		200	0
nickel	sulfur + 50% sand	80	100
		75	20
		70	80
potassium	sulfur + 50% sand	10	10
		7.5	60
		5	20
potassium	wood meal + 50% sand	20	100
		15	60
		10	0
potassium ^f	sulfur	35	80
		30	0
potassium ^{f, g}	sulfur	35	100
		30	80
		25	20
potassium	sulfur	100	100
		75	60
		50	20
strontium	sulfur + 50% sand	20	80
		15	40
		10	20

^a All tests made with 5-kg weight; sample wrapped in 2 x 2 in. lead foil (0.0015 in. thick) unless otherwise specified.

^b All mixtures contain just enough oxygen for complete oxidation, assuming metallic chloride and SO₂ or CO₂ or H₂O as products.

^c Temperature 22 to 28°C unless otherwise specified.

^d S assumed to be oxidized to SO₄.

^e Sample confined by plunger in 1-in. diameter cylinder.

^f Sample confined in brass cup with tight-fitting plunger (0.3 in. diameter).

^g Temperature 90°C.

decomposed when heated to about 335 to 340°C in a test tube, but when confined in a nickel bomb it exploded violently at the same temperature. The kindling temperature was lowered by addition of ammonium perchlorate, and the speed of burning was increased when it was heated on iron or lead, and particularly on copper or zinc or their alloys. Decomposition of equimolar mixtures of pyridine perchlorate and ammonium perchlorate was catalyzed by copper, platinum, platinum oxide, and mercury. The ignition temperature was lowered to 200°C by palladium, cuprous and cupric oxides, brass, a 1:1:1 mixture of $\text{CuO}:\text{Cu}:\text{ZnSO}_4$, and the copper-pyridine complex.

Moureu and Munsch⁷⁴ also studied the properties of pyridine perchlorate because of the reported explosions. They found, as had Arndt and Sevrge,³ that the salt could be detonated by a blow from a hammer. They could not, however, detonate the material by application of energetic friction, and it was decomposed quietly, without explosion, by mineral acid. When subjected to a flame, a small amount of pyridine perchlorate burned with deflagration but exploded only once in 35 attempts. The effect of the crystal size of the salt was not clear-cut, while the presence of added alcohol, ether or perchloric acid did not appreciably modify its behavior to fire or shock in 10 trials. It was concluded that explosions may be due to chlorate present as an impurity.

Trimethylamine oxide perchlorate, $(\text{CH}_3)_3\text{NOHClO}_4$, explodes when heated or struck; *p*-phenylenediamine perchlorate was said (in 1910) to be the most explosive substance known.⁴³ The violet salt, tritolyamine perchlorate, $(\text{CH}_3\text{C}_6\text{H}_4)_3\text{NClO}_4$, melts at 123°C and explodes if heated above this temperature.^{104, 105}

Glasner and Makovsky³⁰ attributed the explosive step of the thermal decomposition of guanidine perchlorate (in the range 345 to 380°C) to the gradual accumulation of perchloric acid parallel with the decrease in concentration of organic matter. While guanidine perchlorate is relatively stable to heat and to mechanical shock, it is reported to be unusually sensitive to initiation and to have extraordinary explosive power.²⁰ The velocity of detonation is about 6000 m/sec at a loading density of 1.15.

The diazonium perchlorates are particularly hazardous, being exploded by the slightest shock when dry. Hofmann and Arnoldi⁴² found that a few centigrams of benzenediazonium perchlorate falling on hard wood tore a deep hole in it, although the explosion was so localized as to leave intact a thin glass vessel 20 cm away. Even when wet with ether, *o*-toluenediazonium perchlorate exploded with great violence under slight pressure from a porcelain spatula. *p*-Toluenediazonium perchlorate was a little less sensitive than the preceding two salts, but both the α - and β -naphthalenediazonium perchlorates exploded violently when dry. *m*-Nitrobenzenediazo-

nium perchlorate exploded spontaneously when heated to about 154°C, and was also sensitive to shock or to a blow.⁴⁰ For use as primers, the maximum detonating power of the aromatic diazoperchlorates was obtained with the mononitro compound.⁴⁰

Of ethyl perchlorate, prepared as long ago as 1841 by Hare and Boye,³⁵ its synthesizers said, "in explosive violence it is not surpassed by any substance known in chemistry." Although this claim is somewhat out of date,⁶⁰ the perchlorate esters are unquestionably of exceptional explosive hazard. The methyl, ethyl and propyl perchlorates are oily liquids which are very sensitive (more than the corresponding nitrate esters) to heat, shock and friction, and extraordinarily explosive.⁷¹ The epichlorohydrin and glycol esters are described as much more explosive than nitroglycerin.⁴⁵ Trichloromethyl perchlorate forms perchloric acid with water; it explodes when heated and, at room temperature, when in contact with alcohol or other organic substances (e.g., stopcock grease).⁸

Partial and complete perchlorate esters with ethylene glycol, glycerine and pentaerythritol were prepared by Zinov'ev *et al*.¹¹⁰ by incremental addition of the alcohol to cooled (−75 to −78°C) anhydrous perchloric acid, followed by heating to 60 to 80°C. These reaction mixtures could not be diluted directly with water, since even a few drops of water caused violent explosions. Dilution was effected by first adding the constant boiling mixture of perchloric acid and water, after which, on addition of water alone, the heavy ester separated from the aqueous solution. The perchlorate ester could then be taken up in diethyl ether in a special apparatus. When conventional separatory funnels were used, explosions occurred which the authors attributed to initiation when the ether extract came into contact with ground glass surfaces. The ether solutions of these esters were found to be considerably more stable than the respective undiluted esters. The partial and complete esters of ethylene glycol and glycerine, obtained as mixtures, were heavy liquids (sp. gr. > 1.7), difficultly soluble in water, and soluble in diethyl ether. The corresponding pentaerythritol esters were colorless solids. All of these esters of polyfunctional alcohols were highly unstable, exploding with great violence upon heating, impact or friction, or even during careful pouring from one container to another.

The alkaryl perchlorates, typical carbonium salts, show a progressive increase in stability as successive hydrogens of the methyl group are replaced by phenyl.¹¹ Benzyl perchlorate appears to be explosive, since an attempt to destroy benzylcelluloses by boiling with perchloric acid resulted in a detonation.⁹⁹

The new perchloryl aromatic compounds are sensitive to shock and heat.^{46, 47, 80} Their properties are described in Chapter 5.

Safe Handling of Perchlorates

From the foregoing discussion, the perchlorates appear to fall into two broad categories: those (1) more or (2) less sensitive to heat and shock. Included in the group of those qualitatively less sensitive are pure ammonium perchlorate, the alkali metal perchlorates, the alkaline earth perchlorates, and perchloryl fluoride. Among the more sensitive compounds are the pure inorganic nitrogenous perchlorates, the heavy metal perchlorates, fluorine perchlorate, the organic perchlorate salts, the perchlorate esters, and mixtures of any perchlorates with organic substances, finely divided metals, or sulfur. Any attempt to establish a more precise order of the degree of hazard to be expected from any given perchlorate seems unwarranted on the basis of the data available. Each perchlorate system must be separately (and cautiously) evaluated. However, it is interesting to speculate on the possibility of developing at least a semiquantitative relationship between the stabilities of the pure perchlorates and their structures, as was suggested for perchloric acid.^{88, 89}

There do not appear to be any uniform recommendations for the safe handling of perchlorates which are generally applicable. As has been shown, a number of the heavy metal and organic perchlorates, as well as hydrazine perchlorate and fluorine perchlorate, are extremely sensitive and must be handled with great caution as initiating explosives. Mixtures of any perchlorates with oxidizable substances are also highly explosive and must be treated accordingly. For all of these, it is essential to avoid friction, heating, sparks, or shock from any source, and to provide suitable isolation, barricades, and protective clothing for personnel. The safety requirements for perchlorate and other propellant mixtures, including plant layout, building design, equipment, operating procedures, storage and transportation, have been summarized by Warren.¹⁰²

The more common ammonium, alkali metal, and alkaline earth perchlorates are considerably less hazardous. Even large quantities may be manufactured in conventional equipment, provided appropriate precautions are taken to avoid overheating or contamination. For example, a number of fires in the drying and packaging equipment of the ammonium perchlorate plant of Western Electrochemical Company (now American Potash & Chemical Corporation) were found to have been caused when the perchlorate crystals came into contact with copper tubing in the vibrating pan-dryer heat exchangers. When stainless steel was substituted for copper the fires ceased.¹ Ammonium perchlorate was found to be most sensitive to ignition at a moisture content of 0.02 to 0.5 per cent, particularly when it is contaminated with copper¹ and possibly in the presence of other metallic contaminants.⁹⁷ This experience confirms other reports of the ac-

celerating effect of copper on the thermal decomposition of ammonium perchlorate⁸² and pyridine perchlorate.⁵⁶ Additional safety precautions taken at the Western Electrochemical Company's ammonium perchlorate plant included rapid drying through the critical range of moisture content, and daily washing of all units of the plant.¹ In the original construction of this plant, flash drying, tunnel drying and packaging operations were housed in individual fireproof units with explosion relief walls. All electrical equipment installed was of explosion-proof design.^{1, 87}

The U. S. Army Ordnance Corps "Ordnance Safety Manual"⁷⁸ includes an excellent summary of the handling and storage requirements for the perchlorates commonly used as oxidants in explosive and propellant compositions (ammonium, alkali metal and alkaline earth perchlorates). The following quotation is from that manual:

1310. OXIDIZING AGENTS

These chemicals which will decompose readily under certain conditions to yield oxygen belong to a class of chemicals called oxidizing agents. The conditions may be elevated temperatures or contact with other chemicals with which they readily react. Examples of inorganic oxidizing agents are the chlorates, perchlorates, peroxides, and nitrates of barium, sodium, potassium, strontium, ammonium, etc. Organic oxidizing agents are often violent explosives and special instructions for their storage and handling should be obtained from the Chief of Ordnance. The following discussion is, therefore, limited to the inorganic oxidizing agents. Oxidizing agents in the pure state present only a fire hazard but because of their ability to furnish oxygen, the hazard is greatly increased and violent explosions may occur when they are mixed or contaminated with even small quantities of certain carbonaceous and combustible materials, such as wood, paper, metal powders, sulfur, etc. The violence of reaction depends upon subdivision, intimacy of mixtures, degree of contamination, degree of confinement and the type initiation afforded. Impregnation of combustible materials including shoes, clothing, etc., with dust or solutions of oxidizing agents is equally dangerous as intimate mixture of finely divided oxidizers and fuels. The mixtures described are very sensitive to heat, friction and impact.

1311. HANDLING OXIDIZING AGENTS

a. Oxidizing agents shall be stored and processed only in rooms or buildings of fire-resistant construction. They shall be separated from supplies of fuels, flammable materials, metal powders and acids until the process requires incorporation. Rooms used for processing oxidizing agents shall not be used for the processing of fuels or combustible materials including metal powders.

b. Equipment for the processing of oxidizing agents shall not be used for the processing of fuels, flammable substances, metal powders, etc. Processing equipment for oxidizers should be constructed of noncombustible materials only.

c. Solutions of oxidizing agents shall be placed only in nonabsorbent and noncombustible containers.

d. Damaged combustible containers shall not be repaired in the storage building because they may be impregnated with oxidizing agent and ignited during repairs. Discarded containers should be burned in the open and should not be sold for other uses.

Combustible containers impregnated with oxidizing agents burn fiercely if ignited and may explode.

e. Employees handling oxidizing agents should wear "flameproof" clothing as a minimum protection. The clothing should be stored in metal cabinets when contaminated. Clothing shall be laundered frequently to minimize the hazard.

f. Spills of small quantities of oxidizing agents during processing must be cleaned up immediately. Such spills shall not be salvaged. If large quantities are spilled, the uppermost layers may be salvaged if there has been no opportunity for it to have become contaminated.

1313. PERCHLORATES

Perchlorates form slightly less sensitive mixtures than do chlorates and should be substituted wherever possible. Advantages of using perchlorates include a lesser sensitivity to impact and friction, the nonformation of a free acid when moisture is present, and greater safety in the event of accidental contact with weak acids which form the principal part of many of the gums such as rosin used in binding pyrotechnic mixtures.

a. Ammonium perchlorate alone is an explosive but is exploded with difficulty. It is stable at ordinary temperatures but decomposes at a maintained temperature of 302°F (150°C). It has the same degree of sensitivity to impact as picric acid. It becomes a high explosive when mixed with flammable materials and metal powders.

b. Containers for perchlorates and chlorates in storage include wooden boxes, kegs, barrels and sometimes iron drums. All damaged and broken containers should be removed from the storehouse and spilled material swept up promptly and destroyed.

c. Fires involving perchlorates alone may be fought with water.

Perchlorates when packed and stored in the original shipping containers or equivalent are considered to be principally fire hazards (Class 1) and no quantity distances are assessed for storage by the Ordnance Corps. When not packed or stored in original shipping containers, perchlorates are included among the Class 2 explosives. Polysulfide-perchlorate propellant compositions containing more than 74 per cent oxidizer by weight are rated at Class 9 explosives. Quantity-distance requirements established by the Ordnance Corps for various classes of explosives may be found in the "Ordnance Safety Manual".⁷⁸ The "American Table of Distances" for the storage of explosives should also be consulted.⁴⁸

Ammonium, barium, potassium and magnesium perchlorates, and other similar perchlorates designated, "Perchlorates, not otherwise specified," are classified by the Interstate Commerce Commission as oxidizing materials—i.e., substances which "yield oxygen readily to stimulate the combustion of organic matter".¹³ The perchlorates in this less hazardous group, in inside containers not over 1 lb net weight each, in outside containers not exceeding 25 lb net weight each, are, unless otherwise provided, exempt from specification packaging, marking, and labeling requirements, except that marking the name of the contents on the outside container is required for shipments via carrier by water. Each outer container for larger quantities than just enumerated must bear the ICC yellow label. The maximum

quantity which may be shipped in one outside container by rail express is 100 lb. By air,⁹⁰ the net quantity allowed per package is 25 lb aboard passenger aircraft, or 100 lb aboard cargo aircraft. Packaging requirements of the Interstate Commerce Commission¹³ are as follows:

Section 73.154—Flammable solids and oxidizing materials not specifically provided for. (a) Flammable solids and oxidizing materials, as defined in Sections 73.150 and 73.151, other than those for which special packing requirements are prescribed, must be packed in specification containers of a design and constructed of materials that will not react dangerously with or be decomposed by the chemical packed therein, as follows:

- (1) Spec. 6A, 6B or 6C. Metal barrels or drums.
- (2) Spec. 17C, 17E, 17H, 37A or 37B, metal drums (single trip).
- (3) Spec. 10A, 10B or 10C. Wooden barrels or kegs.
- (4) Spec. 11A. Wooden barrels or kegs with inside containers, or with suitable lining for bulk shipments.
- (5) Spec. 11B. Wooden barrels or kegs with inside containers, or metal lined, spec. 2F, for bulk shipments.
- (6) Spec. 12B. Fiberboard boxes with inside containers which must be metal cans; sliding-lid wooden boxes; fiber cans or boxes, spec. 2G, not over 5 pounds capacity each; or glass bottles not over 1 pound capacity each. Packages containing glass containers must not weigh over 65 pounds gross.
- (7) Spec. 15A or 15B. Wooden boxes lined, spec. 2F or 2M.
- (8) Spec. 15A, 15B, 15C, 16A, or 19A. Wooden boxes with inside containers.
- (9) Spec. 21A or 21B. Fiber drums.
- (10) Spec. 22A. Plywood drums.
- (11) Spec. 22B. Plywood drums with inside metal drums spec. 2F.

For potassium perchlorate, Section 73.219 of ICC tariff No. 10 also provides for the use of tight bags which will not permit sifting in transit.¹³ Note that most states follow the ICC regulations in controlling the intra-state shipment of hazardous substances.

U. S. Coast Guard regulations¹⁰⁰ covering dangerous articles on board vessels are similar to the ICC requirements for ammonium, barium, magnesium and potassium perchlorates, and "not otherwise specified" perchlorates of like degree of hazard. Storage on cargo vessels is "on deck protected," "on deck under cover," "tween decks readily accessible," or "under deck but not overstowed." The first two of these methods also apply to passenger vessels. Aboard passenger or vehicle ferry vessels, "ferry storage (AA)" is permitted; aboard passenger or vehicle railroad car ferries, "ferry storage (BB)" is specified.

Attention must be called to the fact that the foregoing applies only to the few perchlorates listed above which are primarily fire hazards in contact with oxidizable substances. The responsibility rests with the shipper to insure that the appropriate packaging procedure and the correct labels are used with perchlorates or perchlorate mixtures of greater hazard.

Since many perchlorates are explosive under ICC definitions, the following section of Tariff No. 10 is pertinent¹³:

Section 73.86—Samples of explosives and explosive articles.

(a) New explosives, including fireworks and explosive devices, other than Army, Navy or Air Corps explosive or chemical ammunition of a security classification, must be examined and approved by the Bureau of Explosives as safe for transportation before being offered for shipment, except that a sample of such explosives, fireworks and explosive devices, not to exceed 5 pounds net weight, may be offered for transportation by carriers by rail freight, highway, or water. For the purpose of Parts 71-78 a new explosive, including fireworks and explosive devices, is the product of a new factory or an explosive or explosive device of an essentially new composition or character made by any factory.

(b) Before being offered for shipment, explosive articles in the experimental state must be made safe by removal of ignition elements or otherwise.

(c) Shipments of samples of explosives, fireworks and explosive devices must be packed, marked, and described as required by this part for the explosive contained therein.

(d) Samples of explosives and explosive articles for transportation by rail freight, rail express, or highway. Samples of explosives (except liquid nitroglycerin), including fireworks and explosive devices for examination in a laboratory only and not intended for use or demonstration, may be offered for transportation by rail freight, rail express, or highway provided they fulfill the following requirements:

(1) Samples of explosives including fireworks and explosive devices for laboratory examination must be packed in well-secured metal cans or glass bottles, or in strong waterproof paper or cardboard packages; each sample must consist of not more than one-half pound of explosive, and the interior package must be placed in sawdust or similar cushioning material, at least 2 inches thick, in a wooden box, spec. 14 or 15A.

(2) Whenever these samples of explosives for laboratory examination are contained in a metal envelope or receptacle, this receptacle must be properly cushioned with sawdust or similar cushioning material in a strong wooden box, and this interior box must be packed in a wooden box, spec. 14 or 15A, with at least 2 inches of cushioning material separating the boxes.

(3) Not more than 100 blasting caps may be shipped in one outside package for laboratory examination, and they must be packed and cushioned as provided in paragraph (d) (2) of this section.

(4) Not more than 20 half-pound samples of explosives for laboratory examination may be packed in one outside package or transported in a single car or vehicle at one time.

(5) The net weight of the explosive contents must be plainly marked by the shipper on the outside of each box offered for transportation.

(6) Label. Each outside package containing samples of explosives for laboratory examination must have securely and conspicuously attached to it a square red label as described in Section 73.411 of this part.

Under the laws and regulations of many states,¹⁶ and in view of the previously noted likelihood of Federal action in this area, an appropriate precautionary label should be affixed to containers of all perchlorates. Each such label should take cognizance of the specific hazards (fire, explosion) to be expected from the individual perchlorate. It is recommended that

these precautionary labels should be developed in accordance with the excellent precepts of the Manufacturing Chemists' Association.⁶³ It is also advisable to affix the same precautionary label to outer shipping containers of perchlorates, in addition to any label warnings required by the Interstate Commerce Commission, or applicable statutes, regulations or ordinances.

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12. EQUILIBRIUM DATA ON AQUEOUS SYSTEMS OF PERCHLORATES

The temperature-solubility relations of the alkali and ammonium perchlorates are given in the following tables of data selected from the literature. Also included are a number of three-component systems composed of these salts together with other alkali compounds such as the chlorides, sulfates, etc. In addition, data for the reciprocal salt-pair $\text{Na}_2\text{SO}_4\text{-NH}_4\cdot\text{ClO}_4\text{-(NH}_4)_2\text{SO}_4\text{-NaClO}_4\text{-H}_2\text{O}$, as published by Freeth,⁶ are shown at two temperatures.

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I. SYSTEM $\text{NaClO}_4\text{-H}_2\text{O}$ (Cornec and Dickely⁴)

Temp. (°C)	Density	Weight Per Cent		Grams NaClO_4 Per 100 Grams H_2O	Solid Phase
		NaClO_4	H_2O		
0	—	62.87	37.13	169.32	$\text{NaClO}_4\cdot\text{H}_2\text{O}$
15	1.663	65.63	34.37	190.95	
25	1.683	67.82	32.18	210.75	
28	1.713	70.38	29.62	237.61	
50	1.749	73.26	26.74	273.97	$\text{NaClO}_4\cdot\text{H}_2\text{O}$
15	1.758	71.68	28.32	253.11	
25	1.757	73.21	26.79	273.27	
38	1.757	72.83	27.17	268.05	
55	1.756	73.94	26.06	283.73	NaClO_4^*
75	1.757	75.01	24.99	300.16	
100	1.758	76.75	23.25	330.11	

* Metastable.

Freeth⁶ gives further data, particularly for the ice field at temperatures below 0°C.

II. SYSTEM $\text{KClO}_4\text{-H}_2\text{O}^*$ (Results of average curves of several authors through Seidell¹¹)

Temp. (°C)	Density	Weight Per Cent		Grams KClO_4 Per 100 Grams H_2O
		KClO_4	H_2O	
0	1.005	0.75	99.25	0.76
10	—	1.05	98.95	1.06
15	1.0076	1.33	98.67	1.35
20	1.0085	1.65	98.35	1.67
25	1.0096	2.03	97.97	2.07
30	—	2.50	97.5	2.57
40	—	3.6	96.4	3.74
50	1.017	4.9	95.1	5.15
60	—	6.8	93.2	7.30
70	—	9.2	90.8	10.1
75	1.036	10.36	89.64	11.56
80	—	11.8	88.2	13.4
90	—	15.0	85.0	17.7
100	1.0681	18.2	81.8	22.25
120	—	25.0	75.0	33.3
140	—	32.5	67.5	48.1
180	—	46.0	54.0	85.2
200	—	52.5	47.5	110.5
225	—	60.0	40.0	150.0
250	—	67.0	33.0	203.0
265	—	70.0	30.0	233.0

* Solid Phase = KClO_4 in all cases.

III. SYSTEM $\text{LiClO}_4\text{-H}_2\text{O}$
 (Simmons and Ropp¹²)

Temp. (°C)	Weight Per Cent		Grams LiClO_4 Per 100 Grams H_2O	Solid Phase
	LiClO_4	H_2O		
0	29.90	70.10	42.65	$\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$
10	32.88	67.12	48.99	
20	35.95	64.05	56.13	
25	37.48	62.52	59.95	
30	38.87	61.13	63.59	
40	41.97	58.03	72.32	
64.6	50.0	50.0	100.00	
77.9	55.0	45.0	122.22	
89.2	60.0	40.0	150.00	
92.3	62.5	37.5	166.67	
94.3	65.0	35.0	185.7	
(m.p.) 95.1	66.32	33.68	196.9	
94.8	66.67	33.33	200.0	
93.2	70.0	30.0	233.3	
92.7	70.3	29.7	236.7	
(t.p.) 92.53	70.33	29.67	237.0	$\text{LiClO}_4 \cdot 3\text{H}_2\text{O} +$ $\text{LiClO}_4 \cdot \text{H}_2\text{O}$
93.2	70.5	29.5	239.0	$\text{LiClO}_4 \cdot \text{H}_2\text{O}$
97.3	71.0	29.0	244.8	
108.9	72.8	27.2	267.6	
120.7	75.0	25.0	300.0	
148.5	85.0	15.0	—	$\text{LiClO}_4 \cdot \text{H}_2\text{O}$
(m.p.) 149.0	85.45	14.55	—	
149.3	87.5	12.5	—	
(t.p.) 145.75	—	—	—	$\text{LiClO}_4 \cdot \text{H}_2\text{O} +$ LiClO_4
167.5	91.04	8.96	—	LiClO_4
172.0	91.11	8.89	—	
(m.p.) 236.0	100.00	0.0	—	

IV. SYSTEM $\text{NH}_4\text{ClO}_4\text{-H}_2\text{O}$
(Mazzucchelli & Rosa⁹; Freeth⁶ in parentheses)

Temp. (°C)	Weight Per Cent		Grams NH_4ClO_4 Per 100 Grams H_2O
	NH_4ClO_4	H_2O	
(eut.) -2.72	9.84 (9.8)	90.16 (90.2)	10.91 (10.86)
0.0	10.73 (10.74)	89.27 (89.26)	12.02 (12.03)
15.2	15.95 —	84.05 —	18.98 —
25.0	19.89 (20.02)	80.11 (79.98)	24.83 (25.03)
34.0	23.32 —	76.68 —	30.41 —
45.1	27.64 (28.02)	72.36 (71.98)	38.20 (38.93)
55.2	31.55 —	68.45 —	46.09 —
65.1	35.37 —	64.63 —	54.73 —
75.0	39.05 (39.45)	60.95 (60.55)	64.07 (65.15)
84.7	42.54 —	57.46 —	74.03 —

Carlson² gives solubility of NH_4ClO_4 from 0 to 107°C on a volume basis (g/100 cc).

V. SYSTEM $\text{NaClO}_4\text{-KClO}_4\text{-H}_2\text{O}$
(Hering⁷)

Temp. (°C)	Grams/100 Grams H_2O		Solid Phases
	KClO_4	NaClO_4	
25	2.07	—	KClO_4
	—	211.0	$\text{NaClO}_4 \cdot \text{H}_2\text{O}$
	0.87	210.0	$\text{KClO}_4 + \text{NaClO}_4 \cdot \text{H}_2\text{O}$
100	22.1	—	KClO_4
	—	329.0	NaClO_4
	9.0	333.0	$\text{NaClO}_4 + \text{KClO}_4$

VI. SYSTEM $\text{NaClO}_4\text{-NaCl-H}_2\text{O}$
(Cornec and Dickely⁴)

Temp. (°C)	Density	Grams/100 Grams H_2O		Solid Phases
		NaClO_4	NaCl	
0	—	39.31	25.44	NaCl
	—	80.15	17.02	
	—	123.38	10.21	$\text{NaCl} + \text{NaClO}_4 \cdot \text{H}_2\text{O}$
	—	157.99	6.70	
	—	169.32	0.0	
15	1.663	190.95	0.0	$\text{NaClO}_4 \cdot \text{H}_2\text{O}$
25	1.683	210.75	0.0	$\text{NaClO}_4 \cdot \text{H}_2\text{O} + \text{NaCl}$
	1.683	207.74	4.27	
38	1.713	237.61	0.0	$\text{NaClO}_4 \cdot \text{H}_2\text{O}$
	1.713	234.97	3.55	$\text{NaClO}_4 \cdot \text{H}_2\text{O} + \text{NaCl}$
50	1.749	273.97	0.0	$\text{NaClO}_4 \cdot \text{H}_2\text{O}$
	1.749	271.08	3.03	$\text{NaClO}_4 \cdot \text{H}_2\text{O} + \text{NaCl}$
55	1.756	283.73	0.0	NaClO_4
	1.755	278.41	2.97	$\text{NaClO}_4 + \text{NaCl}$
75	1.757	300.16	0.0	NaClO_4
	1.757	296.36	3.32	$\text{NaClO}_4 + \text{NaCl}$
100	1.758	330.11	0.0	NaClO_4
	1.757	324.86	3.77	$\text{NaClO}_4 + \text{NaCl}$
	1.664	237.07	4.92	NaCl
	1.532	107.54	6.55	
	1.567	83.30	17.71	

VII. SYSTEM $\text{NaClO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$
(Freeth⁶)

Temp. (°C)	Grams/100 Grams H_2O		Solid Phases
	NaClO_4	Na_2SO_4	
25	208.64	0.0	$\text{NaClO}_4 \cdot \text{H}_2\text{O}$
	206.94	0.80	$\text{NaClO}_4 \cdot \text{H}_2\text{O} + \text{Na}_2\text{SO}_4$
	118.59	2.74	Na_2SO_4
	77.13	7.92	
	52.34	15.20	$\text{Na}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
	27.24	18.28	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
	7.61	23.87	
	0.0	27.73	
60	289.11	0.0	NaClO_4
	293.96	1.15	$\text{NaClO}_4 + \text{Na}_2\text{SO}_4$
	184.82	1.06	Na_2SO_4
	113.03	2.39	
	51.30	11.30	
	25.15	21.91	
	0.0	45.35	

VIII. SYSTEM $\text{KClO}_4\text{-KCl-H}_2\text{O}$
 (Benrath and Braun²,)

Temp. (°C)	Grams/100 Grams H_2O		Solid Phases
	KCl	KClO_4	
150	69.55	6.08	KCl
	70.16	9.28	
	65.06	20.82	
	66.48	21.85	$\text{KCl} + \text{KClO}_4$
	60.33	22.49	
	43.16	29.49	
	39.02	29.90	KClO_4
	26.53	39.30	
	18.78	42.82	
175	69.62	10.75	KCl
	72.81	13.41	
	68.38	36.96	
	68.75	39.58	$\text{KCl} + \text{KClO}_4$
	19.54	70.21	KClO_4
200	77.92	10.75	KCl
	79.18	24.90	
	76.45	34.74	
	76.01	48.21	
	72.36	52.36	
	53.71	71.01	KClO_4
	49.55	75.68	
	25.33	93.01	
	24.89	99.33	
225	84.31	33.55	KCl
	77.60	82.81	
	76.96	94.04	
	75.14	107.34	$\text{KCl} + \text{KClO}_4$
	76.74	113.95	
	74.29	111.43	KClO_4
	40.80	126.94	
	30.85	141.19	
250	93.01	25.33	KCl
	95.87	33.49	
	92.41	69.37	
	84.86	76.24	
	79.54	150.50	
	80.81	155.89	$\text{KCl} + \text{KClO}_4$
	48.92	188.00	KClO_4
(Data by Benrath ¹)			
75	48.58	2.29	$\text{KCl} + \alpha \text{KClO}_4$
100	52.09	5.29	
150	58.69	13.43	
200	75.37	35.16	
250	110.95	77.23	

IX. SYSTEM $\text{KClO}_4\text{-NaCl-H}_2\text{O}$ (Internal Ternary System)
(Corneć and Neumeister⁵)

Temp. (°C)	Density	Grams/100 Grams H_2O		Solid Phases
		KClO_4	NaCl	
0	1.005	0.76	0.0	KClO_4
	1.214	1.01	35.86	$\text{KClO}_4 + \text{NaCl}$
	1.209	0.0	35.9	NaCl
25	1.013	2.07	0.0	KClO_4
	1.207	2.22	35.73	$\text{KClO}_4 + \text{NaCl}$
	1.198	0.0	36.3	NaCl
50	1.017	4.95	0.0	KClO_4
	1.205	4.50	36.52	$\text{KClO}_4 + \text{NaCl}$
	1.85	0.0	36.8	NaCl
75	1.036	11.55	0.0	KClO_4
	1.207	9.32	41.47	$\text{KClO}_4 + \text{NaCl}$
	1.176	0.0	37.9	NaCl
100	1.068	22.2	0.0	KClO_4
	1.116	19.75	10.44	
	1.153	17.60	20.75	
	1.190	15.92	30.81	
	1.216	14.51	38.37	$\text{KClO}_4 + \text{NaCl}$
	1.201	11.99	62.99	
	1.183	5.10	38.87	NaCl
	1.164	0.0	40.0	

X. SYSTEM $\text{NaClO}_4\text{-NH}_4\text{ClO}_4\text{-H}_2\text{O}$
(Freeth⁶)

Temp. (°C)	Grams/100 Grams H_2O		Solid Phases
	NaClO_4	NH_4ClO_4	
25	0.0	25.0	NH_4ClO_4
	12.28	19.92	
	40.01	14.77	
	84.75	9.46	
	121.13	8.02	$\text{NH}_4\text{ClO}_4 + \text{NaClO}_4 \cdot \text{H}_2\text{O}$ $\text{NaClO}_4 \cdot \text{H}_2\text{O}$
	217.0	4.86	
	208.6	0.0	
60	0.0	50.6	NH_4ClO_4
	19.96	41.67	
	43.86	31.58	
	74.50	25.02	
	154.97	17.14	$\text{NH}_4\text{ClO}_4 + \text{NaClO}_4$ NaClO_4
	288.33	7.40	
	289.11	0.00	

XI. SYSTEM $\text{NH}_4\text{ClO}_4\text{-(NH}_4)_2\text{SO}_4\text{-H}_2\text{O}$
 (Freeth⁶)

Temp. (°C)	Grams/100 Grams H_2O		Solid Phases
	$(\text{NH}_4)_2\text{SO}_4$	NH_4ClO_4	
25	0.0	25.03	NH_4ClO_4
	14.59	17.29	
	32.35	11.74	
	54.53	6.85	
	75.41	5.42	$\text{NH}_4\text{ClO}_4 + (\text{NH}_4)_2\text{SO}_4$
	76.55	2.18	
	77.00	0.0	
60	0.0	50.6	NH_4ClO_4
	10.60	43.01	
	18.81	39.41	
	27.07	35.13	
	40.00	28.72	
	54.42	22.26	$\text{NH}_4\text{ClO}_4 + (\text{NH}_4)_2\text{SO}_4$
	80.42	16.12	
	84.20	6.64	
	87.97	0.0	

 XII. SYSTEM $\text{NH}_4\text{ClO}_4\text{-NH}_4\text{OH-H}_2\text{O}^*$
 (Kolthoff and Stenger⁸)

Density	Grams/100 Grams H_2O	
	NH_3^\dagger	NH_4ClO_4
1.095	0.0	24.44
1.092	0.87	24.92
1.089	1.75	25.69
1.088	2.64	26.76
1.086	3.42	27.72
1.084	5.50	30.20

* Solubility of NH_4ClO_4 in NH_4OH Solutions at 25°C.

† NH_3 in excess of that present as NH_4ClO_4 .

XIII. SYSTEM $\text{NH}_4\text{ClO}_4\text{-NaCl-H}_2\text{O}$ (Internal Ternary System)
(Schumacher and Stern¹³)

Temp. (°C)	Grams/100 Grams H_2O		Solid Phase
	NaCl	NH_4ClO_4	
25	0.09	25.2	NH_4ClO_4
	7.16	25.0	
	13.9	22.6	
	21.5	21.5	
	30.0	20.0	
	35.15	20.3	$\text{NaCl, NH}_4\text{ClO}_4$
	35.4	14.2	
	35.2	5.8	NaCl
	35.9	0.0	
50	1.0	41.8	NH_4ClO_4
	13.3	38.3	
	19.2	36.6	
	30.2	35.8	
	35.4	32.5	$\text{NaCl, NH}_4\text{ClO}_4$
	36.2	26.8	
	36.2	10.8	NaCl
	36.1	0.0	
80	0.0	66.7	NH_4ClO_4
	21.1	60.4	
	29.6	58.5	
	35.45	57.45	$\text{NaCl, NH}_4\text{ClO}_4$
	36.7	10.6	
	37.6	0.0	NaCl

XIV. SYSTEM $\text{NH}_4\text{ClO}_4\text{-NaHCO}_3\text{-H}_2\text{O}$ (Internal Ternary System)
(Reburn¹⁰)

Temp. (°C)	Grams/100 Grams H_2O		Solid Phase
	NH_4ClO_4	NaHCO_3	
0	12.02	0.0	NH_4ClO_4
	13.04	7.57	NH_4ClO_4 , NaHCO_3
	0.0	7.0	NaHCO_3
20	21.8	0.0	NH_4ClO_4
	23.19	10.77	NH_4ClO_4 , NaHCO_3
	0.0	9.6	NaHCO_3
30	27.9	0.0	NH_4ClO_4
	30.21	12.91	NH_4ClO_4 , NaHCO_3
	0.0	11.1	NaHCO_3
40	34.2	0.0	NH_4ClO_4
	36.43	14.74	NH_4ClO_4 , NaHCO_3
	0.0	12.7	NaHCO_3
50	42.0	0.0	NH_4ClO_4
	45.90	17.55	NH_4ClO_4 , NaHCO_3
	0.0	14.4	NaHCO_3
60	50.2	0.0	NH_4ClO_4
	57.61	21.76	NH_4ClO_4 , NaHCO_3
	0.0	16.0	NaHCO_3

XV. SYSTEM $\text{LiClO}_4\text{-NaCl-H}_2\text{O}$ (Internal Ternary System)
 (Reburn¹⁰)

Temp. (°C)	Grams/100 Grams H_2O		Solid Phase
	LiClO_4	NaCl	
20	0.0	35.87*	NaCl
	30.39	26.92	
	49.89	22.02	
	51.42	14.94	$\text{NaCl} + \text{LiClO}_4 \cdot 3\text{H}_2\text{O}$
	52.83	8.23	
	56.13	0.0	
40	0.0	36.37*	NaCl
	47.53	23.38	
	68.86	19.18	
	68.83	14.66	$\text{NaCl} + \text{LiClO}_4 \cdot 3\text{H}_2\text{O}$
	69.14	6.76	
	72.32	0.0	
60	0.0	37.12*	NaCl
	36.83	26.49	
	63.15	21.22	
	92.56	16.56	$\text{NaCl} + \text{LiClO}_4 \cdot 3\text{H}_2\text{O}$
	90.78	11.36	
	90.40	6.42	
80	93.80	0.0	$\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$
	0.0	38.03*	
	30.52	29.25	
	66.74	21.90	NaCl
	107.7	16.8	
	133.5	15.3	
	129.2	10.75	$\text{NaCl} + \text{LiClO}_4 \cdot 3\text{H}_2\text{O}$
	126.4	5.50	
	126.2	0.0	

* NaCl points from Seidell.¹¹

XVI-A. SYSTEM $\text{Na}_2\text{SO}_4\text{-NH}_4\text{ClO}_4\text{-(NH}_4)_2\text{SO}_4\text{-NaClO}_4\text{-H}_2\text{O}$: Temperature, 25°C
(Freeth⁶)

Grams/100 Grams H_2O				Solid Phases
Na_2SO_4	NaClO_4	$(\text{NH}_4)_2\text{SO}_4$	NH_4ClO_4	
0.0	0.0	75.5	5.43	$(\text{NH}_4)_2\text{SO}_4 + \text{NH}_4\text{ClO}_4$
6.39	0.0	72.86	4.99	
12.94	0.0	70.40	5.01	$(\text{NH}_4)_2\text{SO}_4 + \text{NH}_4\text{ClO}_4 + \text{D}^*$
15.4	0.0	72.9	0.0	$(\text{NH}_4)_2\text{SO}_4 + \text{D}$
12.84	0.0	70.85	4.29	$\text{NH}_4\text{ClO}_4 + \text{D}$
17.35	0.0	54.21	5.01	
24.73	0.0	37.82	5.86	
36.32	0.0	23.47	6.77	
40.90	0.0	19.45	7.36	$\text{NH}_4\text{ClO}_4 + \text{D} + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
42.8	0.0	23.4	0.0	$\text{D} + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
41.42	0.0	21.81	2.65	
17.14	0.0	50.35	6.71	NH_4ClO_4
37.52	0.0	10.54	12.53	$\text{NH}_4\text{ClO}_4 + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
35.03	0.0	0.0	21.02	
25.42	20.48	0.0	15.15	
18.58	41.96	0.0	11.58	
15.2	52.2	0.0	0.0	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$
13.41	58.12	0.0	10.30	$\text{NH}_4\text{ClO}_4 + \text{Na}_2\text{SO}_4(?)$
0.81	211.0	0.0	0.0	$\text{Na}_2\text{SO}_4 + \text{NaClO}_4 \cdot \text{H}_2\text{O}$
0.0	217.0	0.0	4.86	$\text{NH}_4\text{ClO}_4 + \text{NaClO}_4 \cdot \text{H}_2\text{O}$
0.65	212.0	0.0	4.76	$\text{NH}_4\text{ClO}_4 + \text{Na}_2\text{SO}_4 + \text{NaClO}_4 \cdot \text{H}_2\text{O}$

* D = Double Salt $\text{Na}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$.

XVI-B. SYSTEM $\text{Na}_2\text{SO}_4\text{-NH}_4\text{ClO}_4\text{-(NH}_4)_2\text{SO}_4\text{-NaClO}_4\text{-H}_2\text{O}$: Temperature, 60°C
(Freeth⁶)

Grams/100 Grams H_2O				Solid Phases
Na_2SO_4	NaClO_4	$(\text{NH}_4)_2\text{SO}_4$	NH_4ClO_4	
0.0	0.0	80.4	16.1	$(\text{NH}_4)_2\text{SO}_4 + \text{NH}_4\text{ClO}_4$
10.22	0.0	78.17	13.74	
17.94	0.0	77.15	13.06	
31.95	0.0	75.91	11.1	$(\text{NH}_4)_2\text{SO}_4 + \text{NH}_4\text{ClO}_4 + \text{Na}_2\text{SO}_4$
32.69	0.0	75.50	5.93	$(\text{NH}_4)_2\text{SO}_4 + \text{Na}_2\text{SO}_4$
34.92	0.0	78.93	0.0	
33.5	0.0	41.4	19.1	$\text{NH}_4\text{ClO}_4 + \text{Na}_2\text{SO}_4$
33.5	0.0	19.2	29.6	
33.1	0.0	0.0	45.1	
22.5	18.7	0.0	38.6	
8.65	50.26	0.0	28.83	
5.64	70.48	0.0	26.03	
3.16	96.7	0.0	19.9	
2.06	159.8	0.0	20.03	
1.12	183.4	0.0	14.96	
0.97	293.0	0.0	7.43	
0.0	288	0.0	7.4	$\text{NH}_4\text{ClO}_4 + \text{NaClO}_4$
1.14	294	0.0	0.0	$\text{Na}_2\text{SO}_4 + \text{NaClO}_4$

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Appendix

STATISTICAL DATA ON PERCHLORATE PRODUCTION

As a matter of interest, the following statistics on the production of perchlorates in various countries are presented in order to show to some extent, at least, the rate at which the industry is expanding. However, since perchlorates are used extensively for military purposes, much of the information regarding these compounds in recent years has been classified and therefore unavailable. Thus, the figures shown in some cases are quite fragmentary in nature.

Production Figures

World Production

prior World War I 2000-3000 tons/year (perchlorates)¹

Germany (Bitterfeld)

during World War I 20,000 tons/year (perchlorates)¹
1946 15 tons/month (sodium perchlorate)²
80 tons/month (potassium perchlorate)²

Italy

during World War I 30 tons/month (perchlorates)³

Sweden (Mansbo)

1894-1920 4147 tons (ammonium perchlorate)⁴
1281 tons (potassium perchlorate)⁴
1905 11 tons (ammonium perchlorate)⁴
1910 215 tons (ammonium perchlorate)⁴
1916 735 tons (ammonium perchlorate)⁴

Sweden (Trollhätten)

1915-present 750 tons/year, capacity (ammonium perchlorate)⁴
475 tons/year, capacity (potassium perchlorate)⁴

U.S. (total)

1908-1910 90 tons/year (potassium perchlorate)⁵
1943 (estimated) 2400 tons (potassium perchlorate)
1951 4370 tons (potassium perchlorate)⁶
387 tons (ammonium perchlorate)
1954 826 tons (potassium perchlorate)⁶
3952 tons (ammonium perchlorate)
1958 (estimate) 7000-8000 tons (ammonium perchlorate)⁷
1958 (capacity) 18,000+ tons (ammonium perchlorate)⁷

U.S. (total) continued

1960-61 (estimated potential demand)	50,000-100,000 tons (ammonium perchlorate) ⁸
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Consumption Figures

Canada

1953	126,000 lbs. (potassium perchlorate used) ⁹
1954	99,000 lbs. (potassium perchlorate used) ⁹
1955	110,000 lbs. (potassium perchlorate used) ⁹
1956	139,000 lbs. (potassium perchlorate used) ⁹

Imports—U.S.

1947	120,640 lbs. (potassium perchlorate) ⁸
1956	347 short tons (chlorate and perchlorate) ¹⁰
1957	369 short tons (chlorate and perchlorate) ¹⁰

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